

Characterization of Organic Compounds from Selected Residential Wood Stoves and Fuels



**A cooperative study between
Environment Canada and the
Hearth Products Association of Canada**

Report ERMD 2000-01
December 2000

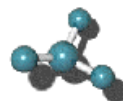
Emissions Research and Measurement Division
Environmental Technology Advancement Directorate



Environment
Canada

Environnement
Canada

**Environmental
Technology
Centre**



**Centre de
Technologie
Environnementale**

Characterization of Organic Compounds from Selected Residential Wood Stoves and Fuels

Notice

This report has been prepared by Environment Canada and reviewed by the Hearth Products Association of Canada. Mention of trade names and commercial products does not constitute recommendation or endorsement for use.

To obtain further information on supporting documentation used to compile this report, please contact:

Dominic Cianciarelli
Emissions Research and Measurement Division
Environmental Technology Centre
Ottawa, ON K1A 0H3

Tel. (613) 991-9457
Fax (613) 998-4032
E-mail Cianciarelli.Dominic@etc.ec.gc.ca

Raouf Morcos
National Office of Pollution Prevention
Place Vincent Massey
Hull, QC K1A 0H3

Tel. (819) 953-1137
Tel. (819) 997-7121
E-mail Raouf.Morcos@ec.gc.ca

Cette publication est aussi disponible en français.

EXECUTIVE SUMMARY

INTRODUCTION

- This is the first Canadian study to compare the releases from a conventional wood stove and a certified (non-catalytic, advanced technology) wood stove for a number of pollutants with a focus on dioxins and furans. The study also verifies the dioxins and furans emission factor used for residential wood combustion (RWC) in the “Inventory of Releases” of dioxins and furans published in 1999 (Environment Canada, 1999).
- The study was jointly carried out by government and industry.
- The need for research in this area became apparent in 1999 when RWC was identified as a major source of dioxins and furans (Environment Canada, 1999). This resulted in RWC being targeted as a priority sector under the Canada-Wide Standards (CWS) process. It was acknowledged, however, that the RWC level-of-activity figure was preliminary and that the emission factor used had been assigned a “low” confidence rating by the U.S. EPA.
- The study was carried out as described in the Quality Assurance Project Plan, prepared by an independent consultant, detailing the steps and procedures that were followed during the stove setup/operation, sampling, analysis and interpretation of the results (Conor Pacific Environmental Technologies Inc., 2000).
- The stoves and wood were chosen and provided by the Hearth Products Association of Canada (HPAC) through consultation between industry and government representatives. It is estimated that the conventional technology wood-burning appliances account for more than 90% of all RWC appliances currently in use. The non-catalytic, advanced technology stove used in the study was a current production model, which is popular across Canada. It is certified as meeting the U.S. EPA particulate emission regulations of less than 7.5 g per hour of operation.
- Environment Canada and HPAC agreed to use two types of wood for this testing program: hard maple which is a common firewood in central and eastern Canada and spruce which is a common softwood species burned in western and northern Canada.
- After a preliminary test run to establish burning rate and minimum volume of sample required for the detection of target compounds, a total of 12 test runs were conducted: three replicate runs with each of the two fuels in each stove.
- The stoves were set up and operated by staff at Intertek Testing Services (ITS) in Montreal according to directions and recommendations from industry and HPAC.
- Intertek Testing Services carried out monitoring for a number of pollutants and provided a report (ITS, 2000).
- Environment Canada scientists carried out the testing in accordance with published methodologies for sampling and analysis.
- In accordance with the Quality Assurance Project Plan, a limited number of samples was sent to an independent laboratory for analysis.
- An independent statistical analysis was performed to determine whether the findings for the dioxins and furans emissions were significant between the stoves and fuels.

CONCLUSIONS

The rigorous approach to test setup and procedure and emission sampling and analysis used in this project produced a high level of confidence in the results of this study.

Under the conditions of this testing program, the results showed the following.

1. Releases of particulate matter (PM), volatile organic compounds (VOCs) and polycyclic aromatic compounds (PAHs) from the certified (non-catalytic, advanced technology) stove are significantly less than those from the conventional stove. On average, releases of these substances from the certified stove are 94% less than those from the conventional stove for PM, 80% for VOCs and 85% for PAHs.
2. Dioxins and Furans
 - a) On a weight-by-weight basis, the average emission factor for residential wood stoves is four times less than the emission factor that was used to develop the dioxins and furans inventory published in January 1999 (Environment Canada, 1999). As a result of the tests and the revision of the quantity of the wood consumed, the release estimates for dioxins and furans from this sector have been reduced from 36.5 to 3 g TEQ/y.
 - b) In both stoves, releases of dioxins and furans from burning maple are higher than those from burning spruce.
 - c) Releases of dioxins and furans from the certified stove are higher than those from the conventional stove.

While a statistical analysis of these results showed that they are representative of the stoves, the fuel and the operating conditions at the time of the test, different conditions during the preliminary test run burning maple in the certified stove produced a result similar to that of the conventional stove during the test program. Unfortunately, little insight was gained into the cause-and-effect relationships that underlie the results for the two stoves and two fuels in this study.

It is clear that more research is required to better determine how dioxins and furans are formed in residential wood-burning equipment.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	ii
LIST OF FIGURES	vi
LIST OF TABLES	vii
ACKNOWLEDGEMENTS	viii
LIST OF ACRONYMS	ix
1. INTRODUCTION	1
1.1 Objective	1
1.2 Summary of Test Program	2
2. SAMPLING SITE AND LOCATIONS	2
3. PROCEDURES	4
3.1 Fuel Preparation and Conditioning	4
3.2 Wood Stove Operation	4
3.3 Combustion Residues	5
3.4 Sampling Methods	5
3.4.1 Particulate	5
3.4.2 Semi-volatile Organic Compounds (SVOCs) Train	5
3.4.3 Volatile Organic Compounds (VOCs)	7
4. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)	8
5. ANALYTICAL METHODS	8
5.1 Particulate	8
5.2 Semi-volatile Organic Compounds (SVOCs)	8
5.3 Volatile Organic Compounds (VOCs)	9
6. RESULTS	10
6.1 Operating Data	10
6.2 Particulate Matter	10
6.3 Dioxins and Furans	11
6.3.1 Particulate/Gaseous Distribution	12
6.3.2 Congener and Homologue Distribution	13
6.3.3 Concentration and Mass Emission Factors	14
6.4 Polycyclic Aromatic Hydrocarbons (PAHs)	15
6.5 Volatile Organic Compounds (VOCs)	15
6.6 Combustion Residues	16
6.7 Propagation of Error	17
6.8 Quality Assurance Samples	18
7. DISCUSSION	18
7.1 Particulate Matter	18

7.2	Dioxins and Furans	19
7.2.1	Concentration and Emission Factors	19
7.2.2	Statistical Analysis.....	21
7.2.3	Other Studies.....	22
7.2.4	Preliminary Run.....	22
7.3	Polycyclic Aromatic Hydrocarbons (PAHs).....	24
7.4	Volatile Organic Compounds (VOCs).....	24
8.	CONCLUSIONS.....	26
9.	REFERENCES	28
 APPENDIX A – DETAILED TABLES		
A-1	Summary of Operating Conditions	30
A-2	Summary of Particulate Matter Emissions (g/kg wood).....	31
A-3	Dioxin and Furan Concentrations (pg TEQ/m ³)	32
A-4	Dioxin and Furan Emission Factors (pg TEQ/kg wood)	33
A-5	PAH Concentrations (µg/m ³).....	34
A-6	PAH Emission Factors (mg/kg wood)	35
A-7	VOC Concentrations (µg/m ³)	36
A-8	VOC Emission Factors (mg/kg wood).....	36
A-9	Propagation of Error Analysis	37

LIST OF FIGURES

	Page
1 General Configuration.....	2
2 Dilution Tunnel Sampling Locations.....	2
3 Semi-volatile Organic Compounds Sampling Train.....	7
4 Volatile Organic Compounds Sampling Train	8
5 Effect of Detection Limit on Average TEQ Train Catch.....	12
6 Average TEQ Distribution of Congeners for Each Test Condition (%).....	13
7 Average Distribution of Homologues for Each Test Condition (%)	13
8 Particulate versus CO in the Dilution Tunnel	19
9 Summary of Dioxin and Furan Concentrations (pg TEQ/m ³)	19
10 Summary of Dioxin and Furan Emission Factors (pg TEQ/kg wood)	20
11 TEQ versus Particulate Matter.....	20
12 Average Dioxin and Furan Emission Factors (ng TEQ/kg wood).....	21
13 Comparison of Average TEQ Emissions with the Preliminary Run	23
14 PAH Emission Factors (mg/kg wood)	24
15 Total VOC Emission Factors (mg/kg wood)	24
16 Selected VOC Emission Factors (mg/kg wood)	25
17 BTEX Emission Factors (mg/kg wood).....	25
18 Relative Emissions of BTEX Compounds (mg/kg wood).....	25
19 1,3-Butadiene Emission Factors (mg/kg wood).....	26
20 Relative Emissions of Target Pollutants	27

LIST OF TABLES

		Page
1	Wood Stove Air Settings	4
2	Wood Stove Operating Sequence	5
3	Summary of Particulate Emission Factors (g/kg wood)	11
4	Summary of Gaseous Fraction of TEQ Dioxins and Furans (%)	12
5	Summary of Dioxin and Furan Concentrations (pg TEQ/m ³)	14
6	Summary of Dioxin and Furan Emission Factors (pg TEQ/kg wood)	14
7	Summary of Gaseous Fraction of PAHs (%)	15
8	Summary of PAH Emission Factors (mg/kg wood)	15
9	Summary of Canister Sampling	16
10	Summary of VOC Emission Factors (mg/kg wood)	17

ACKNOWLEDGEMENTS

Environment Canada acknowledges and appreciates the participation, cooperation and support of the following organizations in this testing program.

- Industry, organized by the Hearth Products Association of Canada.
- Intertek Testing Services.
- Ontario Ministry of the Environment.
- Canadian Council of Ministers of the Environment (CCME) – Canada-Wide Standards Dioxins and Furans Development Committee.

LIST OF ACRONYMS

AAQD	Analysis and Air Quality Division
ASTM	American Society for Testing and Materials
CAEAL	Canadian Association of Environmental Analytical Laboratories
CWS	Canada-Wide Standards
EC	Environment Canada
ERMD	Emissions Research and Measurement Division
ETC	Environmental Technology Centre
GC-MSD	Gas Chromatograph - Mass Selective Detector
HCB	Hexachlorobenzene
HPAC	Hearth Products Association of Canada
I-TEF	International Toxic Equivalency Factor
ITS	Intertek Testing Services
LIMS	Laboratory Information Management System
ND	Non-detectable
OCDDs	Octachlorinated dibenzo-p-dioxins
OCDFs	Octachlorinated dibenzofurans
PAHs	Polycyclic Aromatic Hydrocarbons
PCDDs	Polychlorinated dibenzo-p-dioxins (dioxins)
PCDFs	Polychlorinated dibenzofurans (furans)
PM	Particulate Matter
QAPP	Quality Assurance Project Plan
RWC	Residential Wood Combustion
SVOCs	Semi-volatile Organic Compounds
TEQ	Toxic Equivalents
U.S. EPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds

1. INTRODUCTION

1.1 Objective

Residential wood combustion (RWC) makes a valuable contribution to Canada's mix of energy use, particularly outside major urban areas. This contribution will become especially important as more understanding is acquired of the potential role of renewable fuels such as wood in meeting Canada's climate change obligations under the Kyoto Protocol.

Residential wood combustion is a significant emitter of dioxins and furans¹ into the atmosphere in Canada. In order to develop a reduction strategy for emissions of dioxins and furans, the average emissions from conventional wood stoves must be compared to those of certified, advanced combustion appliances. (Note: In this report, we will refer to this stove simply as the "certified stove".) Little data exists on emissions of dioxins and furans from residential wood stoves, fireplaces and furnaces, and the emission factor previously used was assigned a "low" confidence rating by the U.S. EPA.

The primary objective of this first Canadian study jointly carried out by government and industry is to:

- compare the releases from a conventional and a certified wood stove for a number of pollutants with a focus on dioxins and furans; and
- verify the dioxin and furan emission factor used for residential wood combustion (RWC) in the "Inventory of Releases" of dioxins and furans (Environment Canada, 1999).

According to survey data developed by Environment Canada in 1995, wood stoves represent about 37% of the wood-burning appliances used in Canada, fireplaces make up about 54% and furnaces and other equipment make up the remaining 9%. Although stoves make up just over one-third of all wood-burning appliances, their use accounts for about 55% of the wood burned because stoves are the most common appliance for wood heating as opposed to fireplaces, which are used more casually.

Conventional wood stoves employ modest or no emission reduction technology. These stoves represent the majority of the Canadian wood stove inventory, many of which were installed during the 80s "off oil" era. Advanced combustion, non-catalytic stoves use reduction designs such as baffles and secondary combustion chambers to achieve emission reductions. The other category of certified, advanced combustion stoves use a catalyst downstream of the firebox to control emissions. Catalytic stoves occupy a smaller proportion of the market in Canada than advanced non-catalytic models. While both categories of advanced stoves represent only about 10% of installed stoves, they make up a significant proportion of new appliances purchased in Canada.

¹ In this report, dioxins and furans mean "polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs)".

1.2 Summary of Test Program

The testing and evaluation program was a joint effort between a number of federal and provincial government organizations and industry stakeholders. Main participants included Environment Canada, Intertek Testing Services NA Ltd. and the Hearth Products Association of Canada (HPAC). The test program measured emissions from the following two wood stoves selected by the industry as representative of those used in Canada:

- a conventional stove model that was one of the most popular in the early 1980s; and
- an advanced combustion, non-catalytic, U.S. EPA-certified wood stove, which is currently among the most popular.

Each of the stoves was tested using two species of wood, hard maple (representative of wood burned in eastern Canada) and black spruce (representative of wood burned in northern and western Canada). Tests were conducted at a single representative burn rate and testing was initiated from a hot start. The testing was carried out in triplicate for each wood stove and each fuel type for a total of 12 burn cycle tests. A preliminary test run was conducted using maple in the certified stove model to evaluate the proposed test setup, operation protocol and the minimum volume of sample required for the detection of target compounds.

Sampling was carried out in the dilution tunnel. In addition to dioxins and furans, samples were collected and analyzed for polycyclic aromatic hydrocarbons (PAHs), hexachlorobenzene (HCB), volatile organic compounds (VOCs) and particulate matter. Samples of the combustion residue were collected and submitted for dioxins/furans and chloride analysis.

2. SAMPLING SITE AND LOCATIONS

A U.S. EPA Method 28 type setup was used in the program. The wood stoves were set up inside the building with the chimney system exhausting to an exterior hood assembly at an overall height of 24 ft consisting of about 6 ft of single-wall black pipe connected to the stove and 16 ft of one-inch wall solid pack chimney. This system allows the products of combustion to cool and mix with the outside air in the dilution tunnel upstream of the sampling port locations. A general configuration of the stove, ductwork and sampling locations is shown in Figure 1.

Sampling was conducted at the exit of the wood stove and at the down flow leg of the dilution tunnel. Carbon dioxide, carbon monoxide and oxygen were measured at both the exit of the stove and in the dilution tunnel. Samples for particulate, semi-volatile organic compounds and volatile organic compounds were extracted from different locations in the dilution tunnel. A schematic of the sampling locations is shown in Figure 2.



3. PROCEDURES

3.1 Fuel Preparation and Conditioning

The wood was cut from dead standing trees, split and conditioned to approximately 20% moisture, wet basis. The firewood pieces were sorted into two size ranges. A steel plate with 3, 5 and 7 in diameter holes was used to separate the two sizes, as follows:

- pieces greater than 3 in and less than 5 in were used for kindling; and
- pieces greater than 5 in and less than 7 in were used for the burn cycles.

Moisture content was determined with a Delmhorst moisture probe meter. The maple was dried in a fan-forced cabinet to reduce moisture content from approximately 30% to approximately 20%. The spruce was air dried to less than 20% moisture. The wood was stored in a temperature and relative humidity controlled room/shed until testing.

3.2 Wood Stove Operation

The units tested were supplied by HPAC. The conventional stove was a 20-year-old, top-flue steel stove, equipped with solid cast iron front doors. The combustion chamber consisted of a single wall construction on all sides except the back which had a double wall for the optional convection blower (not used for the tests). The second stove was a top-flue, non-catalytic steel unit meeting the U.S. EPA emission requirements. The combustion chamber was surrounded on all sides except the front with heat shields and the front-loading door was cast iron with a glass panel. As the conventional stove had been in use for several years, no pre-burn period was necessary to condition the unit. However, the certified wood stove was submitted to a break-in period of around 50 hours before testing, which is the U.S. EPA standard procedure for testing wood stoves. Before each test series, the chimney system and laboratory dilution tunnel were cleaned using a standard wire chimney brush.

The wood stove air intake settings used for each test condition were visually determined to correspond to typical fire intensity for home heating. These settings are shown in Table 1.

Table 1 Wood Stove Air Settings

Stove	Maple	Spruce
Conventional	1½ turns from closed position	1 turn from closed position
Certified	¼ open from closed position	3/16 open from closed position

The routine for the operation of each unit was determined prior to the testing program. Loading and operation sequences for each of the stoves are described in Table 2. The test load was added about 100 minutes after light-up, with sampling commencing about five minutes later. The pre-test and test loads (weight, length and moisture) are detailed in the Intertek Report (ITS, 2000).

Table 2 Wood Stove Operating Sequence

Certified	Conventional
Start the fire with kindling and 5 sheets of uncoloured crumpled newspaper.	
Leave door open to set the kindling on fire.	
Close the door with the air intake fully open.	
Add the pretest load and close the door immediately.	
Set the air intake to ¼ (maple) or 3/16 (spruce) of its full range.	Set the air intake 1½ turns (maple) or 1 turn (spruce) open from closing position.
Stir the fire.	
Add the test load and close the door with air intake fully open.	Add the test load and leave the door open.
Start sampling.	
Set the air intake to ½ (maple and spruce).	Close the door with air intake fully open.
Set the air intake to ¼ (maple) or 3/16 (spruce) of its full range.	Set the air intake to 1½ turns (maple) or one turn (spruce) open from closing position.
Stop the test after 4 hours of burn time.	

3.3 Combustion Residues

The unburned residues, composed of inorganic ash and char, were left in the stove for the three triplicate runs. All the residue was collected into amber glass jars 96 hours following completion of the third run. Thus, one composite sample per fuel type, per wood stove was collected and analyzed for dioxins, furans and chloride. Sample preparation of the residue was carried out following ASTM Method D2013-86 (ASTM, 1994). The char pieces in the residue were ground and added to the inorganic ash prior to splitting. Four aliquots (approximately 250 mL each) were prepared for each test condition. Chloride analysis was determined by ion chromatography.

3.4 Sampling Methods

3.4.1 Particulate Particulate matter sampling was carried out following a modified version of U.S. EPA Method 5G (U.S. EPA, 1996), the methodology used by U.S. EPA for the certification of new wood stoves. Replicate particulate samples were collected for each of the test runs. The particulate method is described in detail in the Intertek program report (ITS, 2000).

3.4.2 Semi-volatile Organic Compounds (SVOCs) Train

3.4.2.1 SVOCs Train Description The train consisted of a heated probe, heated filter enclosure, leak-free vacuum line, vacuum gauge, flow control valves, vacuum pump and a dry gas and orifice meter. Dilution tunnel and orifice pressures were measured with an inclined manometer. Temperatures were measured in the hot box, at the impinger train outlet and at the inlet and outlet of the dry gas meter. In the case of the SVOCs, the temperature was also monitored at the Amberlite XAD-2 inlet. All trains were assembled on site in the ERMD mobile lab.

Leak-checks were conducted at the beginning and end of each run or whenever a train joint was opened. Sampling was conducted proportionally from a single point. Readings were recorded every ten minutes over the sampling duration of four hours. This permitted the collection of approximately 5.8 m³ of sample.

Environment Canada's sampling method was used to determine the emissions of dioxins, furans, HCB and PAHs from the dilution tunnel (Environment Canada, 1989). This is the most widely accepted method for measuring organic compounds with boiling points above 100°C. Gaseous organics were trapped in a single adsorbent tube containing about 40 g of Amberlite XAD-2 resin. The EC method is equivalent to the U.S. EPA Method 23.

As the temperature of the resin must be kept below 20°C for optimal collection efficiency, the hot gases leaving the filter enclosure were cooled by passing them through a condenser cooled with ice bath water. The tube containing the XAD-2 resin was also water-cooled. Condensate formed in the cooling coil percolated through the resin bed and was collected in a condensate trap. An impinger containing ethylene glycol inserted downstream of the Amberlite acted as a backup collection media in the event of breakthrough of organics through the resin. The resin tube was covered with aluminum foil during sampling and storage to prevent photodegradation of the trapped organics. All glassware joints were wrapped with Teflon tape as vacuum greases are not permitted for organic sampling. A schematic of the sampling train is shown in Figure 3.

3.4.2.2 Glassware Cleaning and Proofing Prior to the test program, all train glassware, probe brushes, glass wool and aluminum foil were cleaned following a rigorous procedure described in Environment Canada (1989). The glassware cleaning procedures were verified by analyzing the proofing rinses for all the sampling trains. Pre-cleaned and proofed commercial sample storage bottles were used for this test. Sixteen complete sets of train glassware were prepared for this program. The XAD-2 was pre-cleaned and analyzed for contamination prior to the survey. All reagents were distilled-in-glass grade. Details of the cleaning and proofing procedures are given in Environment Canada (1989).

3.4.2.3 Sample Recovery Following the completion of each run, the organic train was recovered in the ERMD mobile laboratory. During transportation between the sampling site and the lab, all openings were sealed with pre-cleaned glass plugs, caps or aluminum foil. The recovery procedures involved brushing and rinsing the train components with acetone and hexane. Only Teflon wash bottles were used during sample recovery. Amberlite tubes were capped and re-wrapped in aluminum foil. Liquid samples were stored in pre-cleaned amber bottles to prevent photodegradation of the organics. Bottle lids were lined with Teflon. All samples were kept refrigerated following recovery. The sample recovery procedures are detailed in Environment Canada (1989). All samples were forwarded to the Analysis and Air Quality Division (AAQD) of Environment Canada for organic analysis. The determination of dioxins and furans from the train samples was carried out in accordance with Environment Canada (1990).

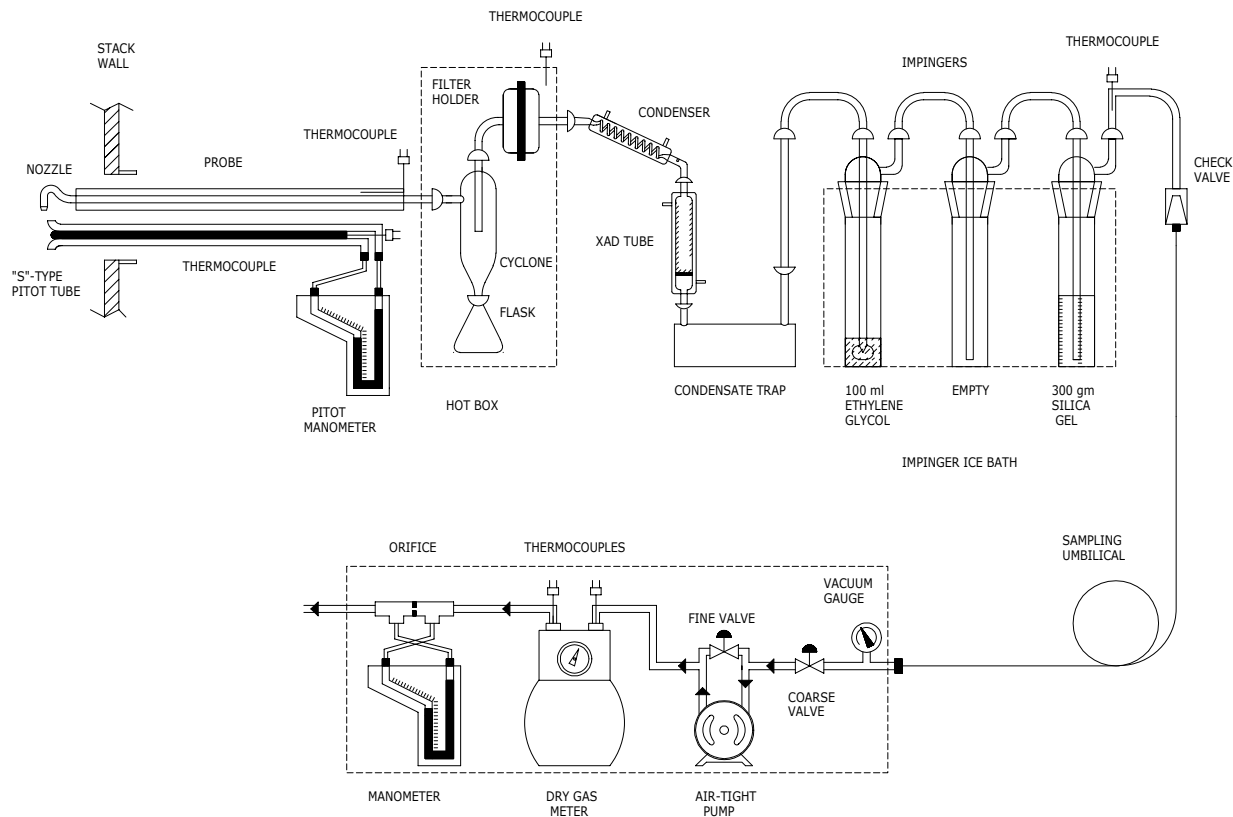


Figure 3 Semi-volatile Organic Compounds Sampling Train

In addition to the regular sampling trains, a blank train was assembled for each test condition. The blank train was treated in the same manner as the sampling trains except that no stack gases were sampled. However, a volume of ambient air equal to that drawn during the leak checks was drawn through the blank train. Essentially, the blank train serves as a check for background levels of organics originating from the handling of train glassware and rinsing agents.

3.4.3 Volatile Organic Compounds (VOCs) Volatile organic compounds are classified as those organics having saturated vapour pressures at 25°C greater than 10^{-1} mm Hg. The method is based on the collection of a gaseous sample in a previously cleaned, proofed and evacuated, 6-L stainless steel canister. The canister's interior surface is covered by pure chrome-nickel oxide, which is formed during the SUMMA® passivating process. This type of vessel provides sample collection and storage stability for many organic compounds. A schematic of the sampling train is shown in Figure 4.

The samples for VOCs were collected in the dilution tunnel. Two to three canisters were collected during each SVOC run. Sampling duration for the VOC samples was variable, ranging from 70 to 80 minutes. The sample was collected into the evacuated canister to a final pressure of 28 to 30 psig. Following sample collection, the canister valve was closed and the canisters were transported to the AAQD laboratory for analysis.

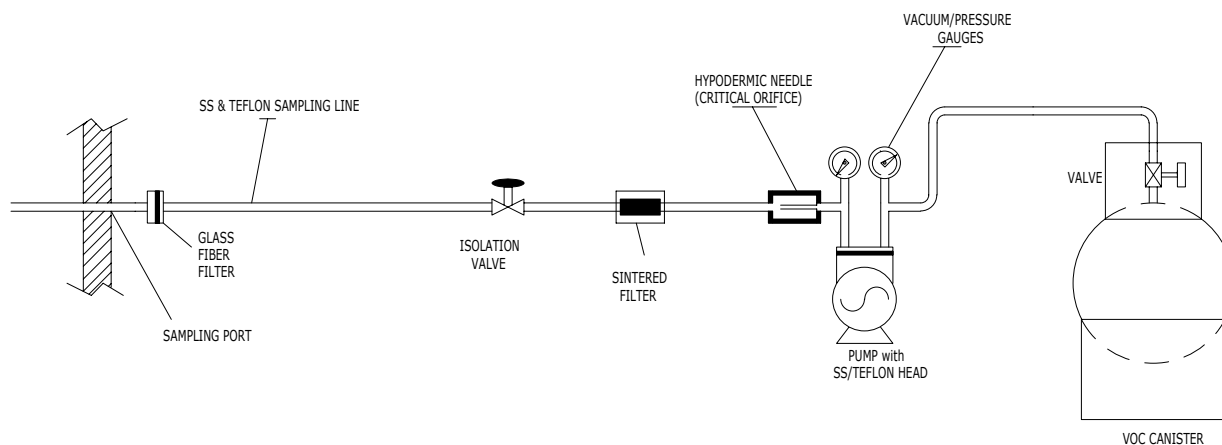


Figure 4 Volatile Organic Compounds Sampling Train

A modified Method TO-15 (U.S. EPA, 1988) was used as the basis for the VOC sampling train. The train consisted of a particulate filter and stainless-steel probe connected by Teflon tubing to the canister. The gases were drawn by a Teflon-coated pump through a critical orifice (hypodermic needle) into the canister (Figure 4).

4. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

A Quality Assurance Project Plan (QAPP) was prepared for the wood stove test program (Conor Pacific Environmental Technologies Inc., 2000). This document details the objectives, activities and specific quality assurance (QA) and quality control (QC) activities as well as data quality objectives for the test program. All activities such as fuel conditioning, wood stove preparation and operation, charging sequences, sampling methodologies, sample integrity and sample analysis are covered in this QAPP.

5. ANALYTICAL METHODS

5.1 Particulate

The emission levels were determined according to Method 5G (U.S. EPA, 1996). Particulate catches were determined gravimetrically.

5.2 Semi-volatile Organic Compounds (SVOCs)

Upon arrival at the laboratory, the samples were inspected to ensure integrity and proper labelling. The samples were then entered into the laboratory information management system (LIMS) where they were assigned a laboratory code. Each container was appropriately coded and stored in a refrigerator at 4°C until sample processing.

The train samples were divided into the front-half (probe rinse, filter and front-half filter holder

rinse) and back-half sections (back-half filter holder rinse, XAD, condensate trap, glycol impinger and back-half glassware rinses). The solvent fractions were dried by passing through sodium sulphate and reduced in volume by rotary evaporation. The solids (filter and XAD) were air dried prior to a 20-hour soxhlet extraction using toluene. Prior to extraction, each sample was spiked with a solution containing a known amount of Carbon-13 labelled dioxins/furans and hexachlorobenzene. These were used to assess losses incurred during the extraction and sample cleanup procedures. Analytical results for dioxins/furans and hexachlorobenzene were corrected for the recovery of these surrogates. After extraction, the solvent extracts of the solids were reduced in volume and combined with the train rinses prior to cleanup. The samples were split into two equal fractions - one was used for PAH cleanup and analysis while the other was used for dioxin/furan and hexachlorobenzene cleanup and analysis.

The dioxins/furans and hexachlorobenzene cleanup is more rigorous since the concentrations of the dioxins/furans are much lower than other compounds that may be present in the extract. These co-extractants could interfere with the final analysis. Initially, the sample extract was passed through a multibed silica column containing layers of acid, base and silver nitrate. Some of the co-extractants were retained on the column, and others were reduced or oxidized. Sulphur-containing compounds were removed by the silver nitrate. The extract was then passed through an alumina column to separate the dioxins/furans from other compounds such as PCBs and hexachlorobenzene. The fraction containing hexachlorobenzene was reduced in volume to 500 µL and an internal standard was added to monitor instrumental performance and was used to correct for any variations in injection and sample volume. The sample was analyzed using low resolution mass spectroscopy. The fraction containing dioxins/furans was reduced to 20 µL and an internal standard was added to monitor instrumental performance and was used to correct for any variations in injection and sample volume. The sample was analyzed using high resolution mass spectroscopy.

As a part of quality assurance and quality control, a method blank containing none of the analytes was processed along with the samples to assess cross-contamination. Environment Canada's Analysis and Air Quality Division participates in interlaboratory studies used to compare results from several different laboratories for various analytes from a variety of matrices. The AAQD is accredited by the Canadian Association of Environmental Analytical Laboratories (CAEAL) for the analysis of dioxins and furans.

5.3 Volatile Organic Compounds (VOCs)

The air samples in canisters were analyzed using a cryogenic preconcentration technique with a high-resolution gas chromatograph and quadrupole mass-selective detector (GC-MSD) as described in U.S. EPA Methods TO-14 and TO-15 (U.S. EPA, 1988). A NuTech model 3550A cryogenic concentrator with autosampler (Model 3600) was used for sample preconcentration. A Hewlett-Packard 5890 series II gas chromatograph and a Hewlett-Packard 5970 MSD instrument were used for speciation and quantification. Volatile organic compounds were separated on a 60-m, 0.32-mm I.D. fused silica capillary column with a 1.0 µm film thickness of J&W DB-1 bonded liquid phase.

Sample gas from the canister was drawn through the preconcentrator's Nafion PermaPure™

dryer to remove water to prevent blockage of the trap and/or capillary column by ice formation at reduced temperature. Sample volumes were measured with a mass flow controller. Normally, 500 mL of ambient air (50 mL for stack sample) was passed through a glass bead trap maintained at -170°C and then a gaseous mixture of internal standard was added directly to the cryogenic trap. The VOCs were back-flushed while being heated to 150°C to be further focused on an open-tubular focusing trap at -180°C . This cryofocusing trap was ballistically heated to 150°C resulting in rapid injection of VOCs onto the analytical column.

Optimum results were obtained by temperature programming the GC column. Column temperature was initially held for 3 minutes at -60°C , and then raised to 250°C at a rate of 8°C per minute. The GC-MSD was operated in the selected ion monitoring mode (SIM). Identification of target analytes by SIM is based on a combination of chromatographic retention time and relative abundance of selected monitored ions. Two or three characteristic ions were monitored for each of approximately 145 hydrocarbon compounds found in urban air samples. Since the MSD acquires data for target ions only, this detection technique is considered highly specific and sensitive. An instrument calibration standard was made from gas standards prepared in the AAQD laboratory from three multi-component liquid mixtures and gas mixture cylinders purchased from Scott Environmental Technology Inc. Quantification was based on five-point linear regression calibration curves.

6. RESULTS

6.1 Operating Data

The general operational data for the tests is summarized in Table A-1 in Appendix A. The fuel and stove exit data was extracted from the Intertek Test Report (ITS, 2000). The fuel charge consisted of five pieces of cordwood. Moisture was measured in each of the five pieces charged into the stove. Moisture values in Table A-1 represent arithmetic averages of the five moisture measurements.

The reporting of the data in this table was limited to those parameters used in the report for the calculation of emission rates and discussion purposes. Emission data is expressed as the mass of pollutant emitted per mass of dry fuel burned during a run. The basis for calculating mass emission rates is four hours. The oxygen, carbon dioxide and carbon monoxide levels reported for the dilution tunnel in Table A-1 represent averages of readings taken every 20 minutes with a Nova Model 376WP combustion gas analyzer.

6.2 Particulate Matter

Particulate results from the Intertek Test Report are reported in Table A-2 in Appendix A. Replicate particulate samples were collected for each run. Samples were collected following Method 5G (U.S. EPA, 1996). Particulate emissions are expressed on the basis of the mass of fuel consumed during the run. An average of the replicate run concentrations and the dilution tunnel flow rate measured by Intertek was used to calculate emission values. Particulate emission factors are summarized in Table 3.

Table 3 Summary of Particulate Emission Factors (g/kg wood)

Stove	Fuel	Range of Emissions	Average
Certified	Maple – TC1*	0.40 - 0.83	0.61
	Spruce – TC2	0.52 - 0.84	0.67
Conventional	Maple – TC3	1.70 - 5.17	2.86
	Spruce – TC4	12.7 - 23.8	17.9

* TC1, TC2, TC3 and TC4 – Test Conditions 1, 2, 3 and 4.

6.3 Dioxins and Furans

Polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD/PCDF) data is reported on the basis of the seventeen 2,3,7,8-substituted dioxin and furan congeners. This data is further transformed by multiplying each of the 17 congeners by their respective international toxic equivalency factors (I-TEFs). The factors range from 1.0 for 2,3,7,8-TCDD to 0.001 for octachlorinated dibenzo-p-dioxins (OCDDs) and octachlorinated dibenzofurans (OCDFs).

Prior to the test program, a preliminary run was conducted at Intertek in Montreal to determine the sample volume required to collect a reliable loading of target analytes. The preliminary run was conducted on the certified stove using maple logs. The operation of the stove during this run was different from the test program in two ways. Two loads of maple were burned in the stove ‘back-to-back’ to extend the operation of the stove in order to collect larger sample volumes. The system height between the floor that the stove was mounted on and the chimney top was 15 ft as per the U.S. EPA wood stove certification setup or about 9 ft shorter than the setup used for the test program. Also, the capture hood for the dilution tunnel was located inside so that ambient indoor air was used for dilution. While the preliminary run was mainly for screening purposes, the results from this run impact on the applicability of the results discussed in Section 7.

Front and back-half components of the SVOC train, which correspond to the particulate and gaseous fractions respectively in the sample gas, were analyzed separately but are reported as train total in the summary tables. Train catches were corrected for the blank train (which consisted solely of OCDD). Concentrations are not corrected to 11% O₂ as the high levels of oxygen measured in the dilution tunnel lead to a large uncertainty of the corrected concentration data.

Two ambient air blanks were collected during the program. Very low levels of dioxins and furans were detected in both of these samples. The maximum possible contribution of ambient air (results not corrected for blanks) was 3 pg TEQ/kg wood for the certified stove and 1 pg/kg wood for the conventional stove. Hexachlorobenzene was analyzed but not reported as the detected levels were at or near the detection limit.

In the analysis of PCDDs/PCDFs using a J&W Scientific DB-5 column (normal practice), other tetra furan isomers may co-elute with the 2,3,7,8-TCDF congener. This means that, when using a DB-5 column, the amounts of this congener may be over-reported. As a result, the analytical laboratory re-analyzed the extracts with a J&W Scientific DB-225 column in order to confirm

the true amount of this congener. This resulted in lower reported quantities of this congener. The DB-225 column data for the 2,3,7,8-TCDF congener was used to determine the TEQ loading. Overall, in terms of TEQ, the contribution of the 2,3,7,8-T4CDF congener with a DB-225 column was reduced to 25% of the DB-5 column. On a test condition basis, the 2,3,7,8-T4CDF TEQ reductions were 27, 29, 24 and 15% for test conditions (TC) 1, 2, 3 and 4 respectively.

Non-detectable (ND) levels were reported for some of the seventeen 2,3,7,8-substituted congeners. There are no steadfast rules for treating NDs. Most often, the treatment of NDs depends upon the jurisdiction and the application of the data. Obviously, the use of the full (100%) detection limit will result in an overestimation of the true value of TEQ. This bias becomes more pronounced with increasing detection limits.

On the other hand, the exclusion of NDs will result in a low estimate of the true total TEQ quantity. For the purpose of reporting emissions, a compromise will be adopted where NDs will be set to 50% of the reported detection limit. The effect of detection limit treatment is shown in Figure 5. However, the NDs will not be considered in the case of particulate/gaseous partitioning and congener distribution. In the case of statistical tests, both scenarios will be presented.

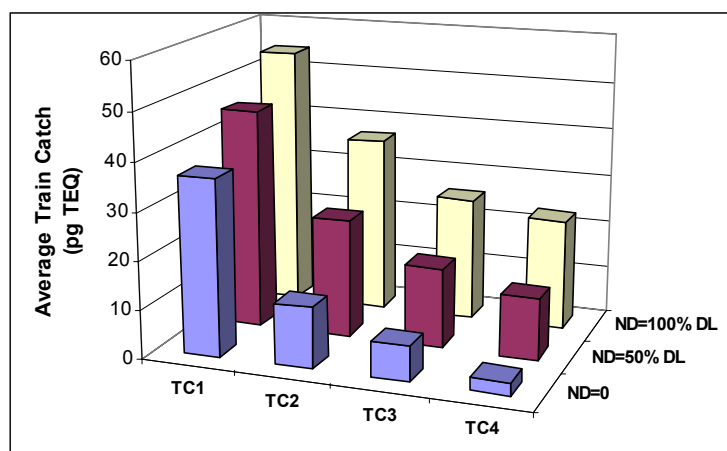


Figure 5 Effect of Detection Limit on Average TEQ Train Catch

6.3.1 Particulate/Gaseous Distribution For the most part, the TEQ dioxins and furans were found in the portion of the sampling train associated with the gaseous fraction. A summary of the gaseous fraction of the total TEQ caught in each train is shown in Table 4.

Table 4 Summary of Gaseous Fraction of TEQ Dioxins and Furans (%)

Stove	Fuel	Run 1	Run 2	Run 3
Certified	Maple – TC1	11	92	99
	Spruce – TC2	100	100	100
Conventional	Maple – TC3	63	100	77
	Spruce – TC4	28	97	49

Distributions were similar among the triplicates for each test condition except for the first run on the certified unit with maple and the first run on the conventional unit with spruce. The higher particulate fraction in the first run (certified unit, maple) was attributable to the 2,3,7,8-T4CDD and the 2,3,4,7,8-P5CDF congeners. This was the only run in which the tetra dioxin congener was detected in the particulate matter. The 2,3,4,7,8-P5CDF congener in the first run

(conventional unit, spruce) accounted for the majority of the congeners detected in the particulate fraction.

The above distributions were based on the exclusion of NDs. Accounting for NDs, whether using one-half or the full detection limit, leads to a bias of particulate/gaseous distributions. This bias is critical since the main objective of this test program is to determine whether a wood stove that emits less particulate also releases less dioxins and furans. The partitioning of the TEQ toward the gaseous phase demonstrates that the release of TEQ from wood stove combustion is unrelated to particulate matter.

6.3.2 Congener and Homologue Distribution

Distribution The average TEQ distribution for the 17 congeners for each test condition is illustrated in Figure 6. The lower chlorinated furans, namely 2,3,7,8-T4CDF and 2,3,4,7,8-P5CDF, accounted for the majority of the detected toxic equivalents. These two congeners accounted for 57, 81, 74 and 72% of the total TEQs for Test Conditions 1, 2, 3 and 4 respectively. Dioxins were present in a few runs. The TEQ contribution of hexa to octa dioxins and furans was minimal for both fractions in all runs.

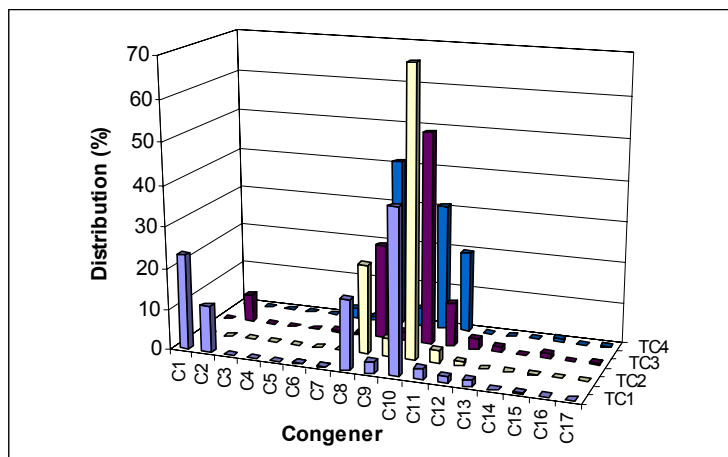


Figure 6 Average TEQ Distribution of Congeners for Each Test Condition (%)

As illustrated in Figure 7, in terms of homologues, most of the detectable dioxins and furans

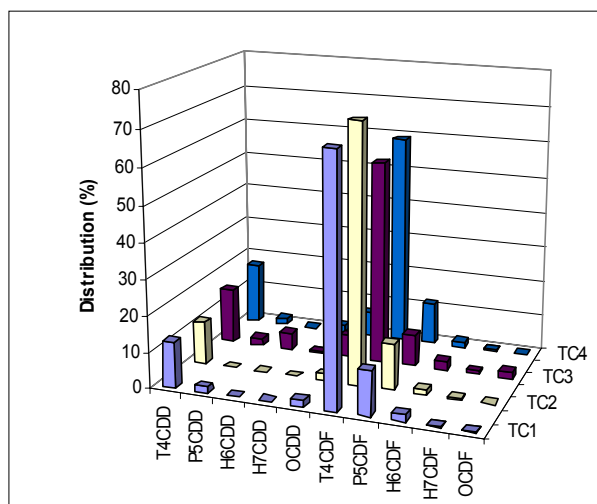


Figure 7 Average Distribution of Homologues for Each Test Condition (%)

resembled the TEQ-weighted congener distribution. While T4CDD was reported in all test conditions, the 2,3,7,8-T4CDD was detected in only three samples, all in the first test condition. On a TEQ basis, the 17 congeners represented 1.9 and 0.7% of the total tetra to octa dioxin and furan homologues for the certified and conventional stoves respectively. On a fuel basis, the 17 congeners represented 1.9 and 0.9% of the total homologues for the maple and spruce respectively for the certified stove compared to 1.0 and 0.4% for the conventional unit.

6.3.3 Concentration and Mass Emission Factors The emission data for the toxic equivalent (TEQ) dioxins and furans measured at the dilution tunnel is given in Table A-3 (concentration) and Table A-4 (emission factors) in Appendix A. The summary of the concentrations of the 17 congeners measured in the dilution tunnel for each run is shown in Table 5. As mentioned earlier, the front- and back-half results are expressed as a train total and the train totals are not corrected to 11% oxygen.

**Table 5 Summary of Dioxin and Furan Concentrations
(pg TEQ/m³)**

Stove	Fuel	Range of Emissions	Average
Certified	Maple – TC1	7.0 - 8.5	7.9
	Spruce – TC2	3.9 - 4.8	4.3
Conventional	Maple – TC3	2.5 - 3.1	2.8
	Spruce – TC4	2.0 - 2.5	2.2

The reporting of the TEQ dioxins and furans on the basis of the fuel consumed (Table 6) offers a normalized basis for the emissions. SVOC samples were collected over a period of four hours. It was assumed that all the fuel was consumed in this period of time. Because of its smaller firebox, fuel consumption in the certified stove was 8.0 to 9.2 kg versus 9.7 to 10.9 kg (dry basis) in the conventional unit.

**Table 6 Summary of Dioxin and Furan Emission Factors
(pg TEQ/kg wood)**

Stove	Fuel	Range of Emissions	Average
Certified	Maple – TC1	850 - 1010	950
	Spruce – TC2	490 - 630	540
Conventional	Maple – TC3	270 - 330	300
	Spruce – TC4	200 - 240	220

The application of 50% of the detection limit for NDs has two effects. Firstly, the addition of ½ NDs reduces the variation between the triplicate values in each test condition. This effect is more evident with the softwood (spruce) in the conventional stove, where the lowest PCDDs/PCDFs were measured. Secondly, the differences between the test conditions are decreased. Again, this effect is exaggerated with the fourth test condition. The effect of NDs on the statistical interpretation of the test data will be discussed in Section 7.

6.4 Polycyclic Aromatic Hydrocarbons (PAHs)

The PAH emissions for all runs are given in Table A-5 (concentration) and Table A-6 (emission factors) in Appendix A. Train catches were corrected for the blank train and the front-and back-half fractions are reported as a single train value. With the exception of 3-methyl-cholanthrene, all the PAH compounds were detected in the samples from each run for both the front- and back-half portions of the train.

Overall, the gaseous fraction of the PAHs (summarized in Table 7) was fairly stable, ranging from 86 to 96% of the total detected in the train. Five compounds (acenaphthylene, fluorene, phenanthrene, fluoranthene and pyrene) accounted for 76 to 91% of the total gaseous portion. Four compounds, representing the heavier fraction of the target PAHs, accounted for the majority of the reported particulate PAHs. These were benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene.

Table 7 Summary of Gaseous Fraction of PAHs (%)

Stove	Fuel	Run 1	Run 2	Run 3
Certified	Maple – TC1	86	93	94
	Spruce – TC2	93	95	96
Conventional	Maple – TC3	92	92	92
	Spruce – TC4	89	90	86

The summary of the PAH emission factors and range of emissions for each test condition is shown in Table 8.

Table 8 Summary of PAH Emission Factors (mg/kg wood)

Stove	Fuel	Range of Emissions	Average
Certified	Maple – TC1	1.2 - 6.3	4
	Spruce – TC2	13 - 25	18
Conventional	Maple – TC3	21 - 26	23
	Spruce – TC4	30 - 62	43

6.5 Volatile Organic Compounds (VOCs)

The full VOC target list contains 144 compounds, however, this list was pared down as many of the species are of lesser interest. Volatile organic compounds of interest include ODS (ozone-depleting substances) such as Freons, BTEX (benzene, ethylbenzene, toluene and xylenes) and halogenated hydrocarbons. Benzene and dichloromethane are identified as CEPA-toxic compounds. An additional VOC (1,3-butadiene) did not fall under any of the above categories, but was added to the reported compounds as it is also classified as a CEPA-toxic compound.

Naphthalene, a PAH compound, was also included since it is not reliably determined using the SVOC Method train.

In this report, Freons and five CEPA-toxic compounds (carbon tetrachloride, vinyl chloride, 1,2-dichloroethane, trichloroethylene and tetrachloroethylene) are not reported as levels detected in the canisters were at ambient air levels. The reported compounds do not include other VOCs of interest such as aldehydes, ketones and alcohols.

At least two canisters were collected for each run for all test conditions. In the case of the conventional stove, three canisters were collected in four of the six runs. A summary of the canister sampling and the sampling duration is given in Table 9.

Table 9 Summary of Canister Sampling

Stove	Fuel	Run 1		Run 2		Run 3	
		Canisters Collected	Duration (min)	Canisters Collected	Duration (min)	Canisters Collected	Duration (min)
Certified	Maple – TC1	2	142	2	140	2	157
	Spruce – TC2	2	157	2	155	2	155
Conventional	Maple – TC3	2	144	3	220	3	221
	Spruce – TC4	3	222	2	151	3	230

Maximum sampling duration per run was 240 minutes.

Canister samples were also collected for ambient air to assess the background contribution of VOCs in the dilution system. Some of the canisters showed elevated levels of VOCs. It is suspected that spill gases from the dilution hood located on the roof were drawn into the inlet hose for the canister, which was situated next to the dilution hood.

Canister results expressed in terms of concentration ($\mu\text{g}/\text{m}^3$) or emission factor (mg/kg wood) are detailed in Table A-7 and Table A-8 respectively (Appendix A). The summary of the total VOC emission factors and range of emissions for each test condition is shown in Table 10. The results are summarized by test condition thus representing an average of either six or eight canisters. As no real-time wood consumption rates were measured during the test program, it was not possible to express VOC emission rates in terms of the fuel consumed over the canister sampling period. Thus emission results were based on an hourly emission rate divided by the average hourly wood consumption. This approach assumes that the emissions are constant over the cycle. This assumption has little impact on the emission data for the conventional stove, since the canisters covered almost all of the burn in four out of six test runs. Unfortunately, it is difficult to quantify the impact of this assumption on the certified stove data.

6.6 Combustion Residues

Four composite samples of combustion residue (ash and char) were submitted for analysis. Two of these samples were submitted for QA analysis. Very low surrogate recoveries were encountered for the PCDDs/PCDFs and PAHs. Residue samples were re-extracted and analyzed but there was no significant improvement in the recovery efficiencies. It is suspected that the

Table 10 Summary of VOC Emission Factors (mg/kg wood)

Stove	Fuel	Average
Certified	Maple – TC1	294
	Spruce – TC2	734
Conventional	Maple – TC3	1072
	Spruce – TC4	4157

poor surrogate recoveries from residue samples were attributable to the presence of elemental carbon. TEQ concentrations ranged from 0.04 to 0.25 pg TEQ/g residue. PAH concentrations ranged from 40 to 529 ng/g residue. Hexachlorobenzene was not detected in any of the combustion residue samples.

6.7 Propagation of Error

The determination of the TEQ involves measuring numerous variables. The reliability of the TEQ value depends on the measured variables. In a propagation of error analysis, the uncertainty of the TEQ emission may be computed using the uncertainties of the individual parameters.

Under Method 5 sampling, where a sample is extracted isokinetically from a source, the determination of the standard reference volume is normally a major contributor to the variance. However, in this program, sampling was conducted proportionally and a steady velocity in the dilution tunnel did not require any change in the sampling rate. This eliminated the uncertainty associated with the measurement of stack gas velocity used to determine the orifice setting required for isokinetic sampling. As such, the effect of the dry gas meter volume was minimized and the variance due to the sample volume was not significant.

The dioxin and furan TEQ mass emission factor was determined using the following equation.

$$EF_{TEQ} = 3600 (U_s)_{avg} A_s (1 - B_{wo}) \frac{T_{ref}}{(T_s)_{avg}} \frac{P_s}{P_{ref}} \frac{W_{TEQ}}{(V_m)_{ref}} \frac{1}{W_w(1-H)}$$

The variance in the mass emission factor was determined with the following equation.

$$\begin{aligned} \left\{ \frac{\sigma_{EF_{TEQ}}}{EF_{TEQ}} \right\}^2 &= \left\{ \frac{\sigma_{(U_s)_{avg}}}{(U_s)_{avg}} \right\}^2 + \left\{ \frac{\sigma_{A_s}}{A_s} \right\}^2 + \left\{ \frac{\sigma_{B_{wo}}}{B_{wo}} \right\}^2 + \left\{ \frac{\sigma_{P_s}}{P_s} \right\}^2 + \left\{ \frac{\sigma_{(T_s)_{avg}}}{(T_s)_{avg}} \right\}^2 \\ &+ \left\{ \frac{\sigma_{W_{TEQ}}}{W_{TEQ}} \right\}^2 + \left\{ \frac{\sigma_{(V_m)_{ref}}}{(V_m)_{ref}} \right\}^2 + \left\{ \frac{\sigma_{W_w}}{W_w} \right\}^2 + \left\{ \frac{\sigma_H}{H} \right\}^2 \end{aligned}$$

The magnitude of each component and the relative contributions are summarized in Table A-9 in Appendix A.

The total variance in the dioxin and furan TEQ mass emission factor is 0.063, which corresponds to a coefficient of variation of 25%. The largest single contributor to the random error was the measurement of the stack gas velocity accounting for 80% of the total variation.

6.8 Quality Assurance Samples

As part of the quality assurance program, train and combustion residue samples were sent to an independent laboratory. Train samples included the front- and back-half components of the second run of the second test condition (certified stove, spruce) and the second run of the third test condition (conventional stove, maple). The QA lab received spiked surrogate extracts. Samples for the second and third test conditions (unspiked) were used for the ash analysis.

Both labs agreed closely on the QA solution for dioxins and furans. With respect to the train samples, the QA lab had better instrument sensitivity and was therefore able to detect many congeners that were reported below the detection limit by the analytical laboratory. Excluding the NDs, the total TEQs for the QA lab were well above the analytical lab. When 100% of the detection limit was applied to the NDs, however, the totals for the analytical lab surpassed the totals reported by the QA lab. Obviously, the congeners were well above 0 but below the detection limits reported by the analytical lab. For this reason, the use of 50% of the detection limit for the treatment of NDs was reasonable and provided a realistic value for the emissions.

TEQ concentrations for dioxins and furans reported by the QA lab were 3.98 and 2.50 pg TEQ/g residue for the second and third test run conditions respectively, versus 0.12 and 0.35 reported by the analytical laboratory. These differences are reduced when 100% of the detection limit is used for NDs.

With respect to PAHs, the results of the four train samples are comparable. The difference between both labs for the QA solution was 30%. In the case of the residue, the QA lab had better recovery efficiencies due to long extraction periods (three days), and was therefore able to detect more PAH compounds.

7. DISCUSSION

7.1 Particulate Matter

In general, there was good accord between the pairs of samples for each run. The emissions of particulate matter varied more among the three runs for each test condition. This is shown in Table A-2 in Appendix A.

Particulate emissions from the U.S. EPA-certified stove were less than from the conventional unit. Particulate emissions for the certified stove were well below 1 g/kg of wood consumed. No

discernible difference was seen between the maple and spruce for the certified stove. While the type of fuel did not affect the particulate emissions from the certified stove, a large difference was noted between the emissions from burning maple and spruce in the conventional stove. Particulate emissions for the softwood fuel (spruce) were approximately six times higher than for the maple.

Figure 8 shows the trend between particulate matter and CO levels in the dilution tunnel. Average CO levels for the certified stove did not exceed 250 ppm. Particulate levels were unaffected by increasing CO levels until approximately 500 ppm, at which point the particulate emissions rose sharply with higher CO levels.

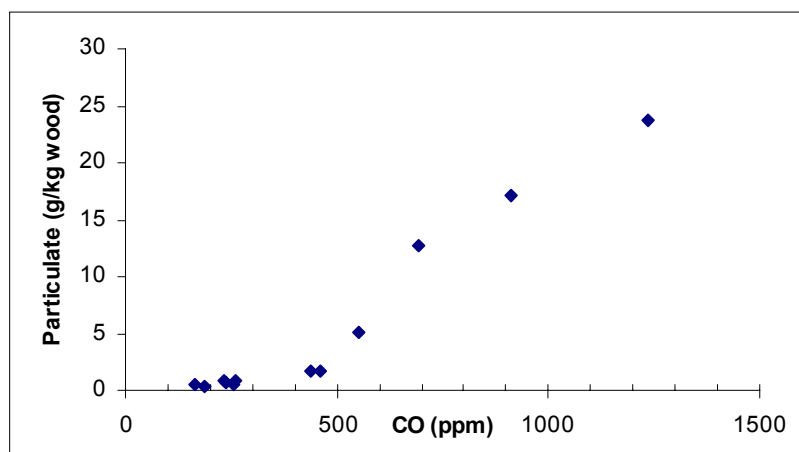


Figure 8 Particulate versus CO in the Dilution Tunnel

7.2 Dioxins and Furans

7.2.1 Concentration and Emission Factors Levels of TEQ for the certified stove were higher than those measured for the conventional unit. Concentrations (Figure 9) ranged from 3.9 to 8.5 pg TEQ/m³ for the certified stove compared to 2.0 to 3.1 pg TEQ/m³ for the conventional stove. TEQ levels for spruce were lower than maple for the certified stove. The difference between the two types of fuel was marginal with the conventional stove. While some of the test conditions exhibited more variation than others, the spread in the triplicate data is considered satisfactory given the nature of the fuel and the operation of the wood stove. The implementation of a documented procedure prior to the test program and the familiarity

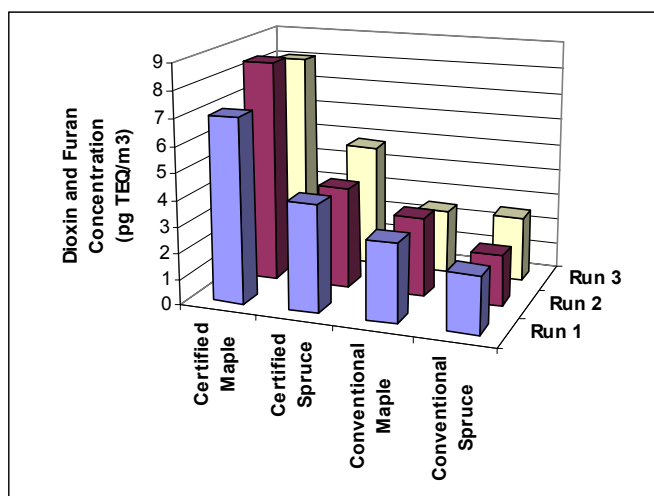


Figure 9 Summary of Dioxin and Furan Concentrations (pg TEQ/m³)

of Intertek with the operation of wood stoves served to minimize the effects of the operator in each test condition.

The differences in the TEQ emission factors between the two fuels and the two wood stoves are shown in Figure 10. The bar graph of the individual TEQ emissions shows that the difference

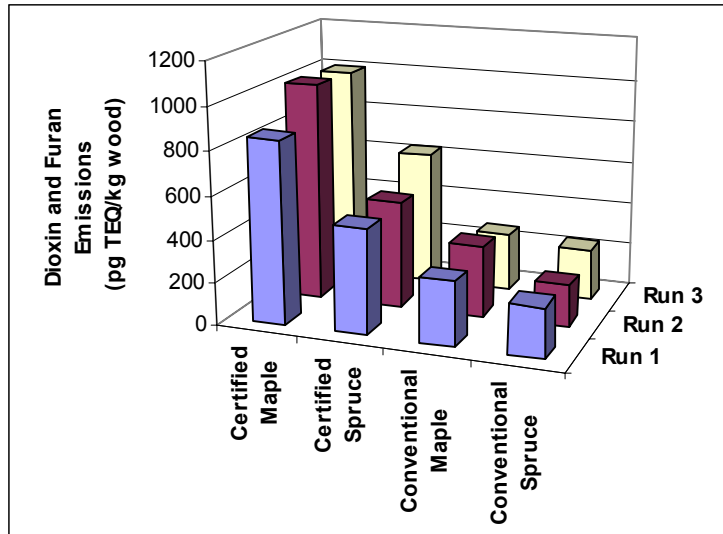


Figure 10 Summary of Dioxin and Furan Emission Factors (pg TEQ/kg wood)

between the two stoves is more obvious when emission data is expressed on a TEQ per mass basis. This is due to the lower charge of fuel for the certified stove. On a mass emission basis, TEQ emissions ranged from 490 to 1010 pg TEQ/kg wood for the certified stove compared to a range of 200 to 330 pg TEQ/kg wood for the conventional unit. Higher emissions were noted with maple than with spruce in the certified unit. Differences between the two fuels burned in the conventional stove were not significant.

One question raised before the study was whether the reduction in particulate from an advanced design of wood stove would result in reduced emissions of dioxins and furans. Stoves were selected that were representative of the two types of appliances burning two types of fuel that are typical of consumption patterns in Canada. The 12 individual readings for the dioxin and furan emission rates are shown in Figure 11. It can be seen that the reduction in particulate matter from the certified stove did not lead to diminished dioxins and furans.

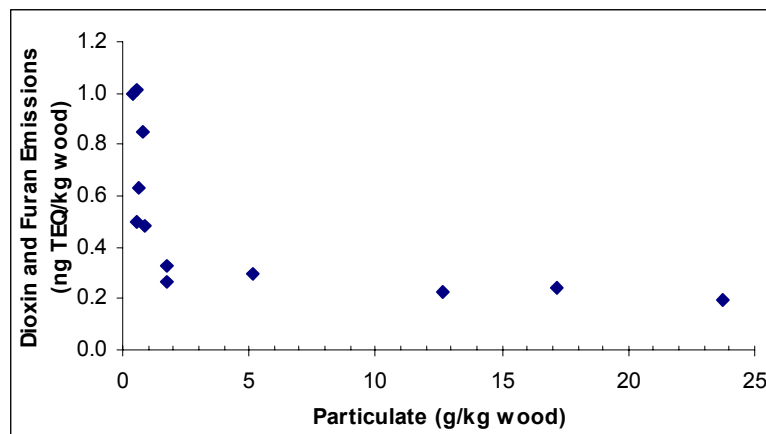
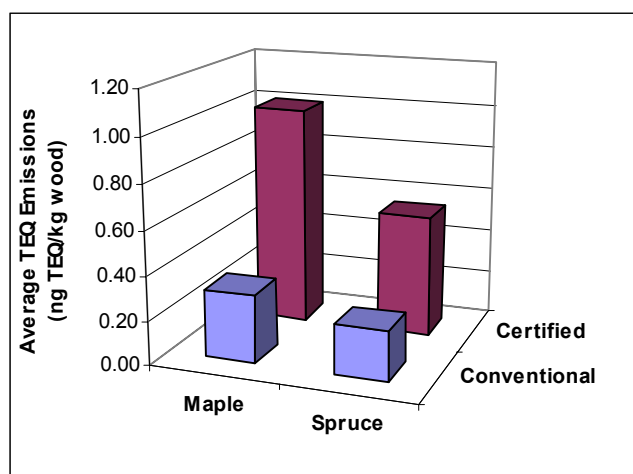


Figure 11 TEQ versus Particulate Matter

The TEQ triplicate averages for each run are shown in Figure 12.

- Emissions from the certified stove are higher than from the conventional stove.
- Emissions from the certified stove when maple was burned were higher than when spruce was burned.
- There was no clear difference in emissions from the conventional stove for the two different fuels.
- The overall emission factor for the four test conditions was 0.5 ng TEQ/kg dry wood.



**Figure 12 Average Dioxin and Furan Emission Factors
(ng TEQ/kg wood)**

7.2.2 Statistical Analysis An independent statistical analysis was performed to determine whether the findings for the dioxin and furan emissions were significant between the stoves and fuels (Zajdlík & Associates, 2000). Two sets of TEQ emission rate data were submitted for analysis. These two sets represented TEQ emissions based on the application of ND=0 and ND=50% of the detection limit.

The relative performance of a stove depends on the type of fuel used. Statistically, this is known as an interaction. The interaction precludes making statements such as stove A produces fewer TEQs than stove B. In this study, conclusions could only be made on the effect of a stove with respect to a certain fuel. Likewise, the same qualification applied to the effect of the fuels on the stoves.

The following are the main conclusions from the statistical analysis.

- The combustion of maple in the certified stove resulted in higher measured TEQs than in the conventional stove, for both methods of dealing with the NDs.
- The combustion of spruce in the certified stove resulted in higher measured TEQs than in the conventional stove, for both methods of dealing with the NDs.
- The combustion of maple in the certified stove resulted in higher measured TEQs than spruce for both ND cases.
- There was no difference in the TEQ emission rate between the maple and the spruce in the conventional stove for both ND cases.

An analysis of variance in the observations indicated that the contribution of the sources of variance (stove, fuel and stove/fuel interaction) was significant for both ND scenarios. In both cases, the stove introduced the largest source of variation followed by the fuel and the stove/fuel interaction. The unexplained variation (residual) was low for both cases compared to these three factors. This reduction in variability increases the statistical power of an experiment and allows for the resolution of smaller differences between means. This suggests that possible effects due to “propagation of error” were negligible given the caveats described in the statistical report (Zajdlik & Associates, 2000).

The statistical analysis showed clear differences between the tested stoves and fuels. Results from the four test conditions were representative of the two stoves, two fuels, test installation and wood stove operation. Are the results obtained in this study extendable to all residential wood stove applications and installations? Unfortunately, very little dioxin/furan emission data is available in the literature to provide a thorough understanding of the parameters of residential wood combustion that affect the levels of dioxins and furans. The existing literature shows that the results for dioxins and furans from residential wood stove combustion are variable.

7.2.3 Other Studies A draft U.S. EPA inventory on residential wood combustion cites two studies in Switzerland and Denmark dealing with dioxins and furans from RWC (Schatowitz et al., 1993 and Vikelsoe et al., 1994). The results from these studies are consistent with the findings of this test program although this program found the emissions to be generally lower. In the Swiss study, combustion of beech firewood resulted in levels of 0.77 to 1.25 ng TEQ/kg wood, corresponding to open-door and closed-door burning conditions respectively.

The Danish study investigated four different stove types burning three different fuels (birch, beech and spruce) under normal and optimal conditions. The operating conditions considered “optimal” by the Danish researchers led to significantly higher PCDD/PCDF emissions for two of the stove types but not for the other two stoves. Emissions from burning spruce were about twice as high as from the beech and birch. The overall emission factor determined in the Danish study was 1.9 ng TEQ/kg wood. It is important to note that the study did not measure the congeners but assumed that the congener distribution was the same as that from municipal waste incinerators.

7.2.4 Preliminary Run The physical configuration of the stove and the venting system and the stove operation may have affected the PCDD/PCDF emissions. This was demonstrated in the preliminary test for this program in December 1999 using the certified stove burning maple. This test was done mainly to determine the sample volume required to obtain a good loading of analyte and to establish an appropriate fuelling and operating protocol.

During the preliminary test, two loads were fed to the stove ‘back-to-back’ to extend the operation of the stove and hence the sample volume. The height of the venting system (the distance between the floor that the stove was mounted on and the chimney top under the dilution hood) was 15 ft, the same as used in the U.S. EPA wood stove certification procedure. In this test program, the height was increased to 24 ft in order to be more representative of the average height of Canadian venting systems. At the same time, this permitted the dilution of the exhaust

gases with outdoor ambient air to represent cooling and mixing conditions of the plume during a Canadian winter.

The results of this preliminary run show that the emission factor (Figure 13) for maple in the certified stove was about 0.29 ng TEQ/kg wood. This value is below the average of Test

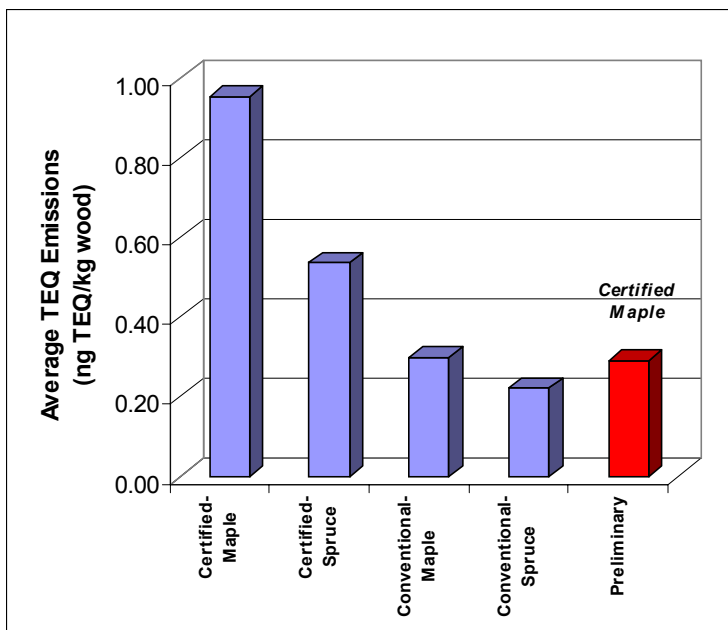


Figure 13 Comparison of Average TEQ Emissions with the Preliminary Run

Condition 1 (0.95 ng TEQ/kg wood) but similar to the maple in the conventional stove measured during Test Condition 3 (0.30 ng TEQ/kg wood).

There is insufficient data from this or other studies to suggest why the emissions produced in the preliminary run were significantly different than those produced during the test program. There were two significant differences between conditions for the preliminary run and the test program, one related to test setup and the other related to stove operation. In the preliminary run, the total height was less and the fuel was burned faster (3 hours per charge versus 4 hours). It could be speculated that one or both of

these differences contributed to the lower emission factor. Other operational differences, the moisture content of the maple and the fact that the stove was new and unconditioned at the time of the preliminary test may also have impacted on the emissions. These factors clearly illustrate the apparent sensitivity of the PCDD/PCDF emissions to the experimental setup, type of fuel and operating protocol.

In general, the results for dioxins and furans from this testing program are representative of the stoves, the wood and the operating conditions at the time of the test. It is possible that the difference between the stoves was true for this study but not necessarily applicable to other scenarios. **Caution must therefore be used in applying the results of this study to advanced and conventional stoves and fuels in general. Clearly, more emission data is necessary to establish differences between the stoves, fuels and operating parameters.**

The Environment Canada inventory (Environment Canada, 1999) used the emission factor given in the Danish study (Vikelse et al., 1994) for estimating the contribution of residential wood-burning emissions of PCDDs/PCDFs to air releases in Canada. Overall, this study shows that the average emission factor for residential wood combustion is about 0.5 ng TEQ per kg of wood. This value is substantially less than the 2 ng TEQ per kg wood emission factor used for the 1999 inventory, which indicates that the contribution of the RWC sector may be overestimated.

7.3 Polycyclic Aromatic Hydrocarbons (PAHs)

A review of the emission values in Figure 14 shows that the conventional stove emitted more PAHs than the certified stove and that emissions when burning spruce were higher than for maple. The higher emissions from the combustion of spruce were more pronounced in the certified stove than in the conventional stove. On average, emissions from burning spruce were quadruple those from burning maple in the certified stove compared to a doubling of PAHs from burning maple as opposed to spruce in the conventional stove. Agreement was variable among the triplicate values for each test condition. In view of the nature of the source and fuel, this variation is considered normal.

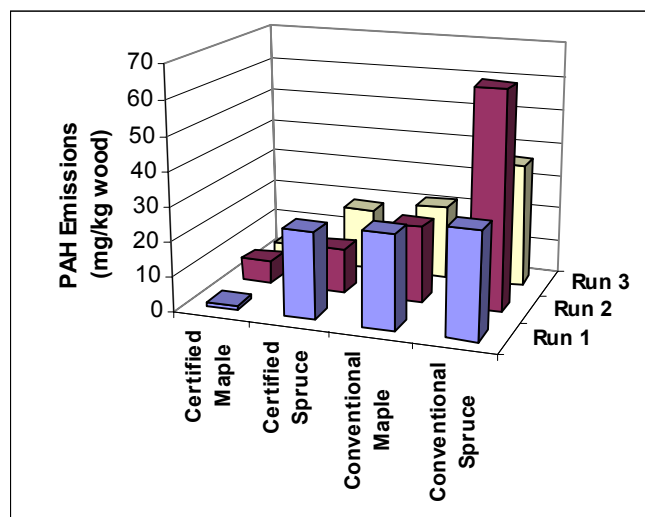


Figure 14 PAH Emission Factors (mg/kg wood)

7.4 Volatile Organic Compounds (VOCs)

A review of the emission profiles for the four test conditions shows two trends (Figure 15). Emissions from the certified stove are less than from the conventional stove and the emissions from burning spruce are greater than maple. In terms of emissions, maple burned in the conventional stove was similar to spruce burned in the certified stove. This trend was also noted in the case of PAHs.

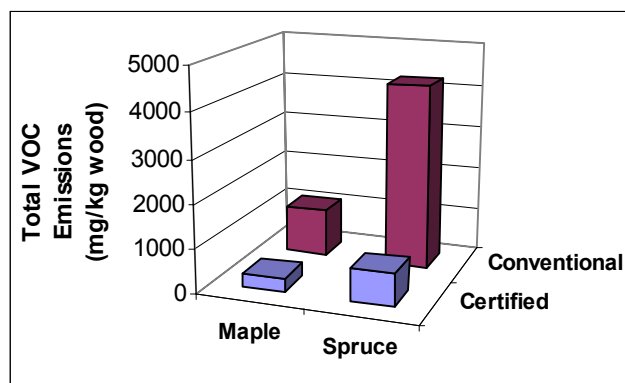


Figure 15 Total VOC Emission Factors (mg/kg wood)

The ten selected VOC compounds (Figure 16) accounted for the majority of the mass of VOCs emitted by the certified unit (58 to 65%). In the case of the conventional stove, the selected VOCs accounted for 29 to 39% of the total. A closer review of the individual VOCs for the conventional stove shows a marked increase of three compounds - propene, propane and 1-butene. These three compounds accounted for 36 and 46% of the total mass of VOCs reported for the conventional stove for the maple and spruce respectively. Benzene and toluene represented the two largest components of the selected VOCs.

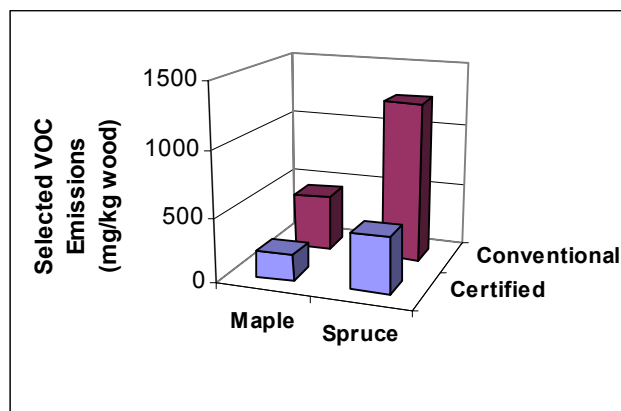


Figure 16 Selected VOC Emission Factors (mg/kg wood)

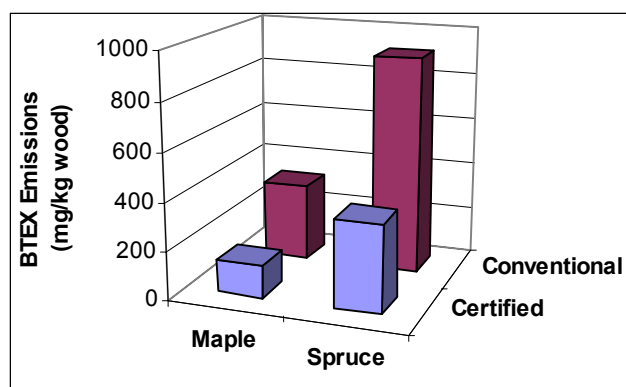


Figure 17 BTEX Emission Factors (mg/kg wood)

Likewise, it can be seen in Figure 17 that total BTEX compounds (benzene, toluene, ethylbenzene and xylenes) are distributed in a manner similar to the selected VOCs. BTEX accounted for the majority of the selected volatile organic compounds. Again, BTEX emissions were similar between Test Conditions 2 (TC2) and 3 (TC3).

The relative emissions of the individual BTEX compounds are shown in Figure 18. Similar emissions were noted for benzene and toluene between TC2 and TC3. The effect of burning spruce in a conventional stove is demonstrated in the figure. Larger increases were noted for ethylbenzene and the xylenes in TC4 (conventional stove, spruce).

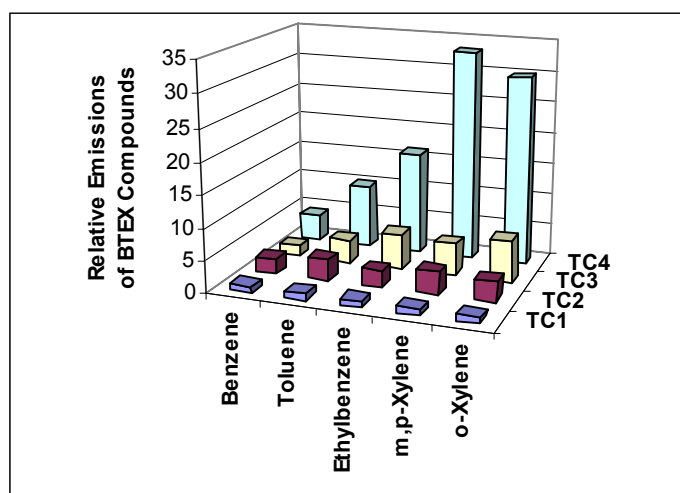


Figure 18 Relative Emissions of BTEX Compounds (mg/kg wood)

Similarly, the level of 1,3-butadiene was higher in the conventional stove, however, the increase in emissions between the two stoves was more pronounced when compared to the BTEX compounds and selected VOCs. This is shown in Figure 19.

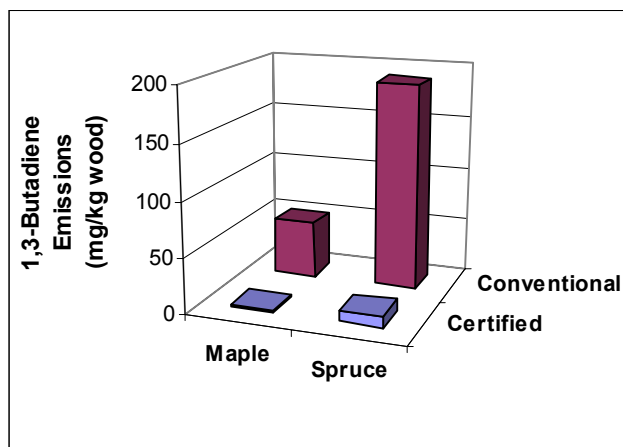


Figure 19 1,3-Butadiene Emission Factors (mg/kg wood)

As mentioned in Section 6.5, some ambient air samples showed elevated levels of VOCs. Volatile organic compounds in the background canisters may have originated from manufacturing plants in the vicinity of the testing facility and/or the stove/dilution hood exhaust. On a concentration basis, the levels of the selected VOCs in the background samples were significant only in the first test condition. More specifically, the background levels for dichloromethane, toluene, ethylbenzene and xylenes were significant compared to the levels found in the dilution tunnel. As the origin of the background VOCs was difficult to establish, it is difficult to assess the impact of these findings on the first test condition. Under the worst case, this means that the reported levels for Test Condition 1 are actually biased on the high side.

8. CONCLUSIONS

The following conclusions are based on the results of this study.

- The certified wood stove (non-catalytic, advanced technology) produced significantly lower emissions of particulate matter, polycyclic aromatic hydrocarbons and volatile organic compounds than the conventional wood stove.
- As a result of this study, it has been demonstrated that the average emission factor for dioxins and furans from residential wood stoves is four times less than the factor used in Environment Canada's inventory report - 0.5 ng TEQ/kg wood instead of 2 ng TEQ/kg (Environment Canada, 1999).
- The certified stove released more dioxins and furans than the conventional stove for each fuel type.
- Dioxin and furan emissions from burning maple were higher than those from spruce for the certified stove.

The close agreement among the triplicate runs and the independent statistical analysis demonstrated that these differences are real and representative of the conditions during the testing.

Using Test Condition 1 (certified unit, maple) as a baseline, the average emissions of the various pollutants for each stove and fuel are expressed as a ratio in Figure 20. Emissions for CO,

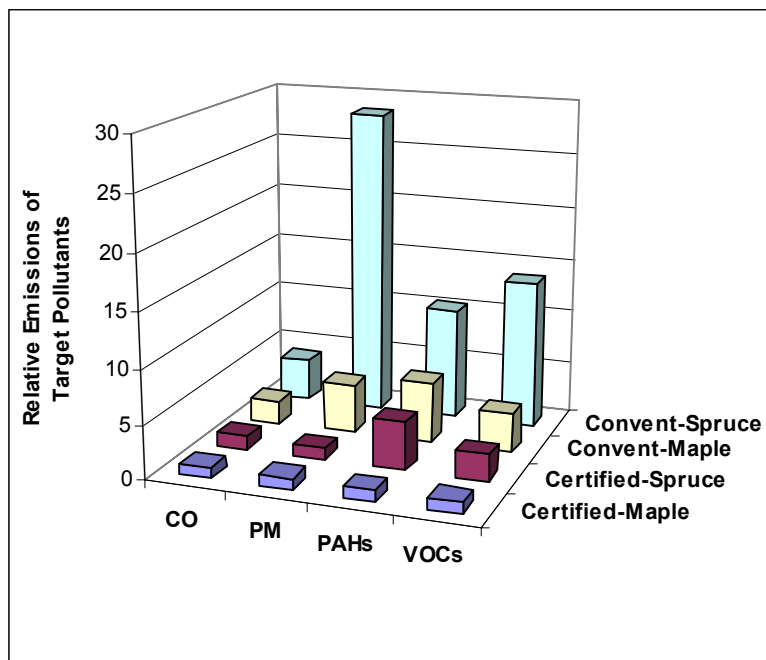


Figure 20 Relative Emissions of Target Pollutants

particulate matter (PM), PAHs and VOCs in the dilution tunnel showed the same trend. The highest emissions were measured from the conventional stove for both the maple and spruce. In contrast to PAHs and VOCs, particulate matter was significantly higher with spruce in the conventional unit, but fuel type did not affect the PM emissions in the certified stove. In general, the increasing formation of PM, PAHs and VOCs with higher CO levels is expected as these compounds are all products of incomplete combustion. Except for particulate matter, the emissions from spruce were higher than maple for each stove type.

Other studies and the result of the preliminary run, however, both contradict and support the findings in this study. This demonstrates that there are other critical factors besides the stove and fuel type that impact upon the emissions of dioxins and furans. **As a result, it would be imprudent to extend the results of this study to all residential wood stove practices. Clearly, more studies are required to obtain a fuller understanding of the factors that affect emissions of dioxins and furans from residential wood stoves.**

The overall emission factor determined from this sequence of tests is significantly reduced from the present value used in the inventory. While applying these results to all situations must be done with caution, it is likely that the overall contribution/impact of dioxin and furan releases in Canada from the residential wood stove combustion sector has diminished.

Although not a part of this test program, it is important to note that other studies have demonstrated that the advanced technology wood stoves are more efficient than conventional stoves. In general, they need less wood to provide the same amount of heat.

As a result of this study, additional testing is required to better understand the formation of

dioxins and furans in residential wood stoves. Among the issues that need to be considered in the design of future studies are the impact of background concentrations of pollutants on the test results, the extraction of target pollutants from elemental carbon, the chimney height and configuration and the wood burn rate.

9. REFERENCES

- ASTM, "Standard Method of Preparing Coal Samples for Analysis", American Society for Testing and Materials, ASTM Method D2013-86, West Conshohocken, PA, approved 1994.
- Conor Pacific Environmental Technologies Inc., "Residential Wood Stove Appliance Test Program, Quality Assurance Plan", CP Project 941-6227, March, 2000.
- Environment Canada, "Dioxins and Furans and Hexachlorobenzene – Inventory of Releases", prepared by Environment Canada and the Federal/Provincial Task Force on Dioxins and Furans for the Federal-Provincial Advisory Committee for the Canadian Environmental Protection Act, Ottawa, ON, 1999.
- Environment Canada, "A Method for the Analysis of Polychlorinated Dibenzo-para-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Polychlorinated Biphenyls (PCBs) in Samples from the Incineration of PCB Waste", Report EPS 1/RM/3 (revised), Ottawa, ON, May, 1990.
- Environment Canada, "Reference Method for Source Testing: Measurement of Releases of Semi-volatile Organic Compounds from Stationary Sources", Report EPS 1/RM/2, Ottawa, ON, June, 1989.
- ITS (Intertek Testing Services), "Test of Two Wood Burning Stoves for Emissions per Highlights of EPA Method 5G-3", Intertek Testing Services NA Ltd., Lachine, QC, 2000.
- Schatowitz, B., G. Brandt, F. Gafner, E. Schlumpf, P. Hasler and T. Nussbaumer, *Organohalogen Compounds*, 11:307-310, 1993.
- U.S. EPA, "Compendium Methods TO-14 and TO-15", *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Second Edition, EPA/625/R-96/010b, 1988.
- U.S. EPA., "Method Determination of Particulate Matter Emissions from Wood Heaters", 40 Code of Federal Regulations (CFR) Part 60, Appendix A, Method 5G, 1996.
- Vikelsee, J., H. Madsen and K. Hansen, *Chemosphere*, Vol. 29, pp. 2019-2027, 1994.
- Zajdlik & Associates, "Analysis of TEQ Emission Rates", prepared for Emissions Research and Measurement Division, Environment Canada, Ottawa, ON, 2000.

APPENDIX A

DETAILED TABLES

Table A-1 Summary of Operating Conditions

Run Number	U.S. EPA-CERTIFIED						CONVENTIONAL					
	Maple (TC1)			Spruce (TC2)			Maple (TC3)			Spruce (TC4)		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Fuel Charge												
Wet Charge (kg)	10.46	10.64	10.68	10.66	9.48	9.17	12.66	11.50	11.62	11.43	11.73	12.16
Number of Pieces	5	5	5	5	5	5	5	5	5	5	5	5
Avg. Moisture (%)	17.5	18.5	18.0	13.8	13.7	13.1	14.2	15.9	15.3	12.4	12.1	12.5
Dry Charge (kg)	8.63	8.67	8.76	9.19	8.18	7.96	10.86	9.67	9.84	10.02	10.31	10.64
Ash Chloride (ppm)	243			104			278			206		
Average Wood Stove Exit – ITS Data												
Temperature (°C)	324	331	336	359	339	337	300	317	278	288	249	288
O ₂ (%)*	14.41	14.60	14.38	13.74	14.68	16.02	13.41	13.66	15.36	10.86	14.35	14.79
CO ₂ (%)*	6.09	5.88	6.07	6.64	5.79	4.56	6.87	7.01	5.06	9.30	5.82	5.54
CO (%)*	0.27	0.24	0.28	0.33	0.24	0.19	0.62	0.48	0.38	1.14	1.09	0.73
Dilution Tunnel (SVOC Sampling Train) – ERMD Data												
Temperature (°C)	13.9	15.3	15.4	21.7	16.2	17.6	15.2	20.3	13.4	13.6	16.5	21.8
Velocity (m/s)	3.80	3.85	4.06	4.13	3.90	3.98	3.97	4.02	3.92	3.85	3.87	3.86
Flow Rate (m³/min)	4.32	4.31	4.51	4.53	4.35	4.37	4.45	4.37	4.50	4.38	4.35	4.23
Sample Volume (m³)	5.786	5.797	5.799	5.798	5.825	5.785	5.810	5.787	5.847	5.804	5.797	5.768
O ₂ (%)*	19.8	20.0	20.1	20.2	19.9	20.2	20.1	19.8	19.9	19.9	20.0	19.9
CO ₂ (%)*	1.13	1.04	0.90	0.90	1.03	0.90	0.97	1.23	1.14	1.07	1.00	0.96
CO (ppm)*	231	162	189	259	254	235	553	436	459	694	1236	910
Moisture (%)	0.63	0.79	0.81	1.04	0.77	0.90	1.00	1.24	0.82	1.10	1.37	1.60

Volumes are expressed on a dry basis, referenced to 25°C and 101.325 kPa.

Wood moisture expressed on a wet basis.

* Dry basis.

Table A-2 Summary of Particulate Matter Emissions (g/kg wood)

Run Number		U.S. EPA-CERTIFIED						CONVENTIONAL					
		Maple (TC1)			Spruce (TC2)			Maple (TC3)			Spruce (TC4)		
		Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Train Data													
Particulate Catch (mg)	Sample 1	4.0	3.8	2.6	5.3	2.9	3.4	31.5	13.4	14.6	103.9	269.5	233.4
	Sample 2	5.1	3.0	1.9	4.7	2.4	3.2	28.2	13.0	14.4	103.3	265.8	232.9
Volume Sampled (ft³)	Sample 1	23.76	24.81	23.07	23.24	22.90	23.37	19.06	28.05	29.13	28.54	36.50	41.22
	Sample 2	22.79	22.64	22.72	22.34	21.77	22.34	16.93	29.33	29.84	28.98	36.38	41.47
Flow Rate (ft³/min)		151.8	148.7	149.6	147.4	149.8	146.5	140.9	149.1	142.6	146.6	139.0	134.8
Particulate Emissions (over 4-hour test period)													
Particulate Emissions (g)	Sample 1	6.13	5.46	4.04	8.07	4.55	5.12	55.90	17.09	17.14	128.08	246.29	183.10
	Sample 2	8.15	4.73	3.00	7.44	3.96	5.03	56.30	15.86	16.51	125.40	243.72	181.61
Average Particulate Emissions (g/kg wood)		0.83	0.59	0.40	0.84	0.52	0.64	5.17	1.70	1.71	12.65	23.77	17.14
Average Particulate Emission per Condition (g/kg wood)		0.61			0.67			2.86			17.85		
Average Particulate Emission per Stove (g/kg wood)		0.64						10.36					

Volumes are expressed on a dry basis, referenced to 25°C and 101.325 kPa.

Fuel expressed on a dry basis.

Table A-3 Dioxin and Furan Concentrations (pg TEQ/m³)
(50% detection limit applied for NDs)

Congener	U.S. EPA-CERTIFIED						CONVENTIONAL					
	Maple (TC1)			Spruce (TC2)			Maple (TC3)			Spruce (TC4)		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
2378-T4CDD	1.76	1.79	2.07	0.69	0.86	0.69	0.69	0.69	0.51	0.60	0.69	0.69
12378-P5CDD	0.90	1.16	0.95	0.34	0.52	0.43	0.34	0.52	0.43	0.26	0.39	0.43
123478-H6CDD	0.17	0.14	0.14	0.09	0.14	0.10	0.09	0.12	0.09	0.07	0.07	0.10
123678-H6CDD	0.17	0.14	0.14	0.09	0.14	0.10	0.09	0.12	0.09	0.07	0.07	0.10
123789-H6CDD	0.17	0.14	0.14	0.09	0.14	0.10	0.09	0.12	0.09	0.07	0.07	0.10
1234678-H7CDD	0.02	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.01
OCDD	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00
2378-T4CDF	1.07	1.12	1.03	0.80	0.37	0.42	0.28	0.35	0.33	0.25	0.16	0.19
12378-P5CDF	0.18	0.20	0.19	0.10	0.10	0.13	0.06	0.04	0.03	0.04	0.02	0.05
23478-P5CDF	2.02	3.11	2.83	1.57	1.17	2.29	0.86	0.72	0.60	0.52	0.17	0.35
123478-H6CDF	0.18	0.26	0.19	0.10	0.10	0.17	0.28	0.11	0.09	0.16	0.07	0.19
123678-H6CDF	0.12	0.15	0.16	0.07	0.10	0.11	0.10	0.07	0.05	0.03	0.07	0.09
234678-H6CDF	0.15	0.14	0.12	0.07	0.10	0.08	0.07	0.07	0.05	0.03	0.07	0.09
123789-H6CDF	0.08	0.08	0.09	0.07	0.10	0.08	0.04	0.07	0.05	0.03	0.07	0.09
1234678-H7CDF	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01
1234789-H7CDF	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01
OCDF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
TOTAL	7.04	8.47	8.07	4.11	3.88	4.77	3.03	3.05	2.45	2.18	1.95	2.51
Average	7.86			4.25			2.84			2.21		

Sample collected in the dilution tunnel. All values are expressed on a dry basis, referenced to 25°C and 101.325 kPa.

**Table A-4 Dioxin and Furan Emission Factors (pg TEQ/kg wood)
(50% detection limit applied for NDs)**

Congener	U.S EPA-CERTIFIED						CONVENTIONAL					
	Maple (TC1)			Spruce (TC2)			Maple (TC3)			Spruce (TC4)		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
2378-T4CDD	212	214	256	82	110	91	68	75	56	63	70	66
12378-P5CDD	108	138	117	41	66	57	34	56	47	27	39	41
123478-H6CDD	21	16	17	10	18	14	8	13	9	7	7	10
123678-H6CDD	21	16	17	10	18	14	8	13	9	7	7	10
123789-H6CDD	21	16	17	10	18	14	8	13	9	7	7	10
1234678-H7CDD	2	2	2	1	2	2	1	1	2	1	2	1
OCDD	1	0	0	0	0	0	0	1	1	0	1	0
2378-T4CDF	129	134	127	95	47	55	28	38	36	27	16	18
12378-P5CDF	22	24	23	12	13	17	6	4	4	5	2	5
23478-P5CDF	243	371	350	186	149	302	85	78	66	54	17	33
123478-H6CDF	22	31	23	12	13	23	27	11	10	16	7	18
123678-H6CDF	15	18	20	8	13	15	10	8	6	4	7	8
234678-H6CDF	17	17	14	8	13	10	7	8	6	4	7	8
123789-H6CDF	10	10	11	8	13	10	4	8	6	4	7	8
1234678-H7CDF	2	1	2	1	2	2	2	2	1	1	1	1
1234789-H7CDF	2	1	1	1	2	2	1	1	1	0	1	1
OCDF	0	0	0	0	0	0	0	1	0	0	0	0
TOTAL	846	1012	998	486	496	628	298	331	269	228	198	240
Average	952			537			299			222		

Sample collected in the dilution tunnel.
Fuel expressed on a dry basis.

Table A-5 PAH Concentrations ($\mu\text{g}/\text{m}^3$)

Compound	U.S. EPA-CERTIFIED						CONVENTIONAL					
	Maple (TC1)			Spruce (TC2)			Maple (TC3)			Spruce (TC4)		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Acenaphthylene	0.9	5.8	2.0	23.4	8.7	20.0	57.4	20.7	28.2	36.9	122.7	64.9
Acenaphthene	0.1	0.5	0.1	1.3	0.5	1.9	6.9	2.1	1.9	5.3	11.8	6.8
Fluorene	0.5	2.6	0.9	9.8	3.7	7.8	23.8	10.7	12.8	24.6	66.5	34.8
2-Methyl-Fluorene	0.1	0.2	0.1	0.6	0.3	0.4	3.6	0.9	1.3	7.0	18.8	10.0
Phenanthrene	4.6	20.0	15.6	60.2	34.3	44.5	67.9	57.2	49.2	83.1	166.9	96.0
Anthracene	0.2	1.8	0.6	10.6	3.4	6.6	15.0	7.7	8.5	13.7	32.3	16.9
Fluoranthene	1.2	7.1	5.8	27.4	14.3	15.4	25.2	28.1	24.0	30.5	47.9	33.5
Pyrene	0.8	6.5	4.6	20.1	9.9	11.3	20.8	22.6	17.6	20.2	38.6	23.2
Benzo(a)Fluorene	0.0	0.7	0.2	2.7	1.3	1.5	3.9	1.9	2.4	4.1	9.6	5.9
Benzo(b)Fluorene	0.0	0.4	0.1	0.9	1.0	0.9	2.4	1.0	1.5	1.8	5.2	2.9
1-Methyl-Pyrene	0.0	0.6	0.2	2.3	0.8	1.7	2.7	1.5	1.5	5.9	14.1	8.4
Benzo(g,h,i)Fluoranthene	0.2	1.2	0.9	4.5	2.2	2.5	3.6	4.4	3.9	4.1	6.4	4.8
Benzo(a)Anthracene	0.1	1.1	0.8	7.3	3.3	3.5	6.4	4.9	5.4	7.9	13.3	10.7
Chrysene	0.2	1.2	0.9	7.2	2.9	3.9	5.2	5.1	5.2	8.0	12.4	10.4
Triphenylene	0.1	0.2	0.2	1.5	0.5	0.5	1.0	0.9	0.9	1.6	1.4	1.1
7-Methyl-Benzo(a)Anthracene	0.0	0.0	0.0	0.1	0.0	0.0	0.2	0.1	0.1	0.4	0.6	0.5
Benzo(b)Fluoranthene	0.3	1.6	1.2	8.6	4.0	4.1	6.3	7.7	6.6	9.1	12.1	12.5
Benzo(k)Fluoranthene	0.1	0.5	0.3	2.4	1.0	1.0	1.8	1.9	1.7	2.3	2.5	2.3
Benzo(e)Pyrene	0.1	0.7	0.5	3.4	1.8	1.6	2.7	3.5	2.9	3.7	5.1	5.0
Benzo(a)Pyrene	0.1	1.1	0.4	5.1	1.9	2.3	5.1	5.2	4.4	6.4	10.2	9.4
Perylene	0.0	0.1	0.1	0.7	0.2	0.3	0.7	0.7	0.6	0.8	1.4	1.3
3-Methyl-Cholanthrene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Indeno(1,2,3-cd)Pyrene	0.2	0.9	0.5	3.1	1.5	1.6	2.6	3.6	3.7	3.8	4.9	4.9
Dibenzo(a,h)Anthracene	0.0	0.1	0.1	0.6	0.2	0.2	0.4	0.5	0.5	0.5	1.0	0.9
Benzo(b)Chrysene	0.0	0.1	0.0	0.4	0.1	0.1	0.4	0.3	0.2	0.4	0.7	0.7
Benzo(g,h,i)Perylene	0.2	0.9	0.5	2.5	1.3	1.4	2.3	3.5	3.9	2.9	4.4	4.2
Anthanthrene	0.0	0.1	0.0	0.4	0.1	0.2	0.8	0.8	0.6	1.0	2.0	1.6
TOTAL	10	53	37	207	99	135	269	198	190	286	613	374
Average	33			147			219			424		

Sample collected in the dilution tunnel. All values are expressed on a dry basis, referenced to 25°C and 101.325 kPa.

Table A-6 PAH Emission Factors (mg/kg wood)

Compound	U.S. EPA-CERTIFIED						CONVENTIONAL					
	Maple (TC1)			Spruce (TC2)			Maple (TC3)			Spruce (TC4)		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Acenaphthylene	0.11	0.69	0.24	2.77	1.11	2.63	5.64	2.25	3.09	3.87	12.44	6.19
Acenaphthene	0.01	0.06	0.01	0.15	0.06	0.25	0.68	0.23	0.20	0.56	1.20	0.65
Fluorene	0.06	0.32	0.11	1.16	0.48	1.03	2.34	1.16	1.41	2.58	6.74	3.32
2-Methyl-Fluorene	0.01	0.02	0.01	0.08	0.04	0.05	0.36	0.10	0.15	0.73	1.90	0.95
Phenanthrene	0.55	2.03	1.93	7.12	4.38	5.86	6.68	6.21	5.40	8.72	16.93	9.16
Anthracene	0.02	0.22	0.07	1.25	0.43	0.87	1.47	0.83	0.93	1.44	3.28	1.62
Fluoranthene	0.15	0.85	0.72	3.24	1.83	2.03	2.47	3.06	2.63	3.20	4.86	3.20
Pyrene	0.10	0.78	0.57	2.38	1.26	1.48	2.04	2.46	1.93	2.12	3.92	2.21
Benzo(a)Fluorene	0.00	0.08	0.03	0.32	0.16	0.20	0.39	0.21	0.27	0.43	0.97	0.56
Benzo(b)Fluorene	0.00	0.05	0.01	0.11	0.12	0.13	0.24	0.11	0.16	0.19	0.53	0.28
1-Methyl-Pyrene	0.00	0.07	0.02	0.27	0.11	0.22	0.27	0.16	0.16	0.61	1.43	0.80
Benzo(g,h,i)Fluoranthene	0.02	0.14	0.11	0.53	0.28	0.33	0.35	0.48	0.43	0.43	0.65	0.45
Benzo(a)Anthracene	0.01	0.14	0.10	0.87	0.42	0.46	0.63	0.53	0.59	0.83	1.34	1.02
Chrysene	0.02	0.14	0.12	0.85	0.37	0.51	0.51	0.55	0.57	0.84	1.26	1.00
Triphenylene	0.01	0.03	0.03	0.18	0.06	0.07	0.09	0.10	0.10	0.17	0.14	0.11
7-Methyl-Benzo(a)Anthracene	0.00	0.00	0.00	0.01	0.00	0.01	0.02	0.01	0.01	0.04	0.06	0.05
Benzo(b)Fluoranthene	0.03	0.19	0.14	1.01	0.52	0.54	0.62	0.84	0.72	0.96	1.23	1.19
Benzo(k)Fluoranthene	0.01	0.06	0.04	0.28	0.13	0.14	0.17	0.21	0.18	0.25	0.26	0.22
Benzo(e)Pyrene	0.02	0.09	0.07	0.40	0.22	0.21	0.27	0.38	0.32	0.39	0.52	0.48
Benzo(a)Pyrene	0.01	0.13	0.05	0.60	0.24	0.31	0.50	0.57	0.48	0.67	1.03	0.89
Perylene	0.00	0.02	0.01	0.08	0.03	0.04	0.07	0.08	0.07	0.09	0.14	0.12
3-Methyl-Cholanthrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Indeno(1,2,3-cd)Pyrene	0.02	0.10	0.06	0.37	0.19	0.21	0.26	0.39	0.41	0.40	0.50	0.47
Dibenzo(a,h)Anthracene	0.00	0.01	0.01	0.07	0.03	0.03	0.04	0.06	0.05	0.06	0.10	0.09
Benzo(b)Chrysene	0.00	0.01	0.00	0.04	0.01	0.02	0.04	0.04	0.03	0.05	0.08	0.07
Benzo(g,h,i)Perylene	0.02	0.11	0.07	0.30	0.16	0.18	0.23	0.38	0.43	0.30	0.45	0.40
Anthanthrene	0.00	0.02	0.00	0.05	0.01	0.02	0.08	0.08	0.06	0.10	0.20	0.15
TOTAL	1.20	6.34	4.53	24.51	12.67	17.80	26.45	21.45	20.80	30.01	62.16	35.65
Average	4.02			18.33			22.90			42.61		

Sample collected in the dilution tunnel.
Fuel expressed on a dry basis.

Table A-7 VOC Concentrations ($\mu\text{g}/\text{m}^3$)

Compound	U.S. EPA-Certified		Conventional	
	Maple (TC1)	Spruce (TC2)	Maple (TC3)	Spruce (TC4)
Chloromethane	10	10	80	52
1,3-butadiene	19	85	496	1884
Dichloromethane	16	9	23	15
Benzene	820	1941	1749	4416
Toluene	213	708	900	2626
Ethylbenzene	23	62	153	470
m,p-xylene	26	91	155	1057
o-xylene	9	29	70	339
Styrene	48	118	169	643
Naphthalene	385	328	206	652
Total Above	1571	3379	4001	12153
Total All VOCs	2428	5848	10185	41377

Sample collected in the dilution tunnel. All values are expressed on a dry basis, referenced to 25°C and 101.325 kPa.

Table A-8 VOC Emission Factors (mg/kg wood)

Compound	U.S. EPA-Certified		Conventional	
	Maple (TC1)	Spruce (TC2)	Maple (TC3)	Spruce (TC4)
Chloromethane	1	1	8	5
1,3-butadiene	2	11	52	189
Dichloromethane	1.9	1.1	2.4	1.5
Benzene	99	244	184	444
Toluene	26	89	95	264
Ethylbenzene	3	8	16	47
m,p-xylene	3	11	16	106
o-xylene	1	4	7	34
Styrene	6	15	18	65
Naphthalene	47	41	22	65
Total Above	190	424	421	1221
Total All VOCs	294	734	1072	4157

*Sample collected in the dilution tunnel.
Fuel expressed on a dry basis.*

Table A-9 Propagation of Error Analysis

Error Term	Magnitude	Contribution to Total Variance (%)
Average Stack Gas Velocity $\{\sigma_{(U_s)_{avg}} / (U_s)_{avg}\}^2$	0.0502	80
Stack Area $\{\sigma_{A_s} / A_s\}^2$	0.00692	11
Stack Gas Moisture $\{\sigma_{B_{wo}} / B_{wo}\}^2$	0.0000257	Negligible
Absolute Stack Gas Pressure $\{\sigma_{P_s} / P_s\}^2$	0.000001	Negligible
Stack Gas Temperature $\{\sigma_{(T_s)_{avg}} / (T_s)_{avg}\}^2$	0.001479	2.4
Mass TEQ $\{\sigma_{W_{TEQ}} / W_{TEQ}\}^2$	0.003824	6.1
Total Sample Volume $\{\sigma_{(V_m)_{ref}} / (V_m)_{ref}\}^2$	0.0004678	0.7
Weight Wood $\{\sigma_{W_w} / W_w\}^2$	0.0000042	Negligible
Humidity of Wood $\{\sigma_H / H\}^2$	0.000041	0.1
Emission Factor $\{\sigma_{EF_{TEQ}} / EF_{TEQ}\}^2$	0.063	100